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Four issues per volume, three volumes per year

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Back numbers, £10 (U.S.A. $28.00) per volume

Single issues, £2. 10s. (U.S.A. $7.00) each

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Geochimica et Cosmochimica Acta, 1961, Vol. 22, p. 1. Pergamon Press Ltd. Printed in Northern Ireland

Foreword

In response to a request by the members of Section I of the Fourth World Petroleum Congress at Rome in 1955, a symposium was organized by the Committee dealing with Resolution 4 of the Third World Petroleum Congress,* on the general theme: "Chemical Approaches to the Recognition of Petroleum Source Rocks". This symposium was held on Wednesday, 3 June 1959, at New York, in connexion with the general sessions of the Fifth World Petroleum Congress.

Interest in this area on the part of the Committee has been a direct outgrowth of its efforts over the past 8 years to define and to characterize the organic matter in sedimentary rocks and, in particular, those rocks which are believed to have yielded petroleum.

Five of the seven papers presented at the symposium are published here as a group. A paper by Dr. P. H. Abelson (Geophysical Laboratory, Carnegie Institution of Washington) on "kerogen", and one by Dr. R. von Gaertner (Amt für Bodenforschung, Hanover) and Professor H. Kroepelin (Technische Hochschule, Braunschweig) dealing with an "investigation on the organic substance contained in the Posidonia-shale of northwest Germany", unfortunately could not be completed for publication at this time.

William E. Hanson
Special Editor of the Symposium

* M. Louis, President of the Committee, Institut Français du Pétrole, Paris, France; E. Eisma, Koninklijke/Shell Laboratory, Amsterdam, The Netherlands; W. E. Hanson, Mellon Institute, Pittsburgh, Pa., U.S.A.; C. F. Jackson, Institute of Petroleum, London, Great Britain; and G. R. Schultze, Institut für Erdölforschung, Hanover, Germany.

Geochimica et Cosmochimica Acta, 1961, Vol. 22, pp. 2 to 15. Pergamon Press Ltd. Printed in Northern Ireland

Distribution of *n*-paraffins as a clue to recognition of source beds

E. E. Bray and E. D. Evans
Magnolia Petroleum Company, Field Research Laboratory, Dallas, Texas

Abstract—A preference for *n*-paraffins with odd numbers of carbon atoms is widespread in Recent sediments. Analyses of numerous Recent sediment samples indicate that molecules with odd numbers of carbon atoms predominate in the heavy *n*-paraffins for at least the first few thousand years after deposition. The depositional environments studied include a continental shelf, some ocean basins, bays, fresh-water lakes, a saline lake and soils. In contrast, the heavy *n*-paraffins in a representative selection of crude oils are evenly distributed between molecules of even- and odd-carbon number.

Analyses of a limited number of postulated source rocks showed no preference in the heavy *n*-paraffins for molecules of either odd- or even-carbon number. Some shales and limestones ranging from Eocene to Mississippian in age have been examined for possible application of the *n*-paraffin distribution to recognition of source beds.

Introduction

Geologists have long recognized the importance of identification of source rocks of petroleum. Although at present there is no completely satisfactory explanation for the origin of petroleum, it has been assumed often that petroleum was generated from source materials during long periods of burial and compaction. There is evidence indicating that large quantities of hydrocarbons have indeed been generated in the sediments during long periods of burial. Buckley *et al.* (1958) made an extensive study of the distribution of dissolved hydrocarbons in subsurface waters of the East Texas and Gulf Coast areas. Methane and heavier hydrocarbons were found at depths below a few thousand feet. The amount of dissolved gas and the percentage of heavier hydrocarbons increased with depth even though the ground water was not saturated in most of the formations studied. Erdman *et al.* (1958) found light aromatic hydrocarbons to be abundant in ancient marine shales and limestones and to be uniformly absent in Recent muds from a variety of environments. These hydrocarbons were apparently formed after considerable depth of burial and compaction. Forsman *et al.* (1958) studied rock samples representing a wide variety of ages, lithologies and environments of deposition. Both the absolute concentrations of hydrocarbons and the concentrations relative to total organic matter were apparently greater in ancient rocks than in Recent sediments.

On the other hand, reports of the occurrence of hydrocarbons in Recent sediments by Smith (1954) gave impetus to an idea earlier proposed by Whitemore (1944) that crude oils result from selective preservation of these naturally occurring hydrocarbons. Baker (1959) has proposed that oils may result from selective accumulation of these hydrocarbons. Reports by Stevens *et al.* (1956), Evans *et al.* (1957) and Meinschein (1958) have shown that though there are similarities between hydrocarbons in some Gulf of Mexico Recent sediments and in petroleum, the relative distributions of hydrocarbon types and molecular size vary considerably. For example molecules with odd numbers of carbon atoms were predominant in the *n*-paraffins of the Recent sediments in contrast to corresponding fractions from crude oils and a petroliferous shale which had no predominance with respect to either odd- or even-carbon numbers.

In this paper, we present *n*-paraffin distribution data for a greater variety of Recent sediments and crude oils than have been published previously and include also similar data for some shales and limestones ranging from Eocene to Mississippian in age. These data are examined for possible application in recognition of source beds.

Description of Samples

Recent sediments

Forty-one Recent sediment samples from marine, bay, fresh-water lake, saline lake and soil environments, were examined (Table 1). Samples from marine environments were obtained by coring the sediments to depths of 30 ft, in some cases. Water depths varied from 30 ft on the Texas and Louisiana Gulf Coasts to over 5000 ft in ocean basins off the shore of Southern California where sediments from the Catalina, San Nicolas, Tanner, West Cortez, Santa Barbara, Santa Cruz and Santa Monica Basins were sampled to depths of 10 ft by use of a gravity coring tool. Recent sediments in these California basins have been adequately described by Emery and Rittenberg (1952).

Samples from bay environments were largely soft to firm muds representing sediments up to 65 ft in depth obtained by coring. The core sites were in the shallow waters of Corpus Christi and Galveston bays on the Texas Gulf Coast.

The lake sediments included corings of soft organic mud from fresh-water lakes in Wisconsin and firm dry sediment from a former saline lake in California. The fresh-water lake samples were obtained from Grassy and Trout lakes of Northern Wisconsin. Sediments ranging from 10 ft to 37 ft in thickness were sampled by corings which penetrated the entire Recent sediment deposits. These sediments have been described by Twenhofel *et al.* (1942, 1945). The saline lake samples were from the 61 to 66 ft interval from Searles Lake located in San Bernardino County, California. Flint and Gale (1958) have described these sediments.

The soils examined were from Texas, Wyoming and Sumatra. These have been previously reported by Meinschein (1958).

Crude oils

Thirty-nine crude oils were selected to represent most of the principal oil-producing areas of the Western Hemisphere (Table 2). The selection includes a wide variety of oils with high, medium and low gravities. The reservoir rocks containing these oils ranged from Pliocene to Cambrian in age.

Ancient sediments

Forty-three samples of fine-grained ancient marine sediments, including shales and a few limestones, were examined (Table 3). Outcrop samples were taken from formations of Cretaceous, Jurassic, Pennsylvanian and Mississippian age in the Big Snowy Mountains of Central Montana. These formations are producing oil at depth within distances of a few miles from the outcrops. Other outcrop samples of marine shales were obtained from the Woodford and Chattanooga formations of Mississippian age in Oklahoma and the Chattanooga near Nashville, Tennessee. Additional samples were taken from shallow coreholes which penetrated to maximum depths of a few hundred feet in outcropping formations of North Central

Table 1. Recent sediments

Location	Description	Water depth (ft)	Depth in sediment (ft)	Ratio odd/even carbon-number
Ocean Basins, Off Shore, Southern California				
Catalina Basin	Olive-brown mud, grey interbeds	4300	1–4	4·9
Catalina Basin	Olive-brown mud, grey interbeds	4300	5–9	5·1
San Nicolas Basin	Olive-brown mud	5300	0–4	2·5
San Nicolas Basin	Olive-brown mud	5300	4–6	2·4
Santa Cruz Basin	Olive-brown mud	5700	1·5–5	3·3
Santa Cruz Basin	Olive-brown mud	5700	5–9	3·6
Santa Monica Basin	Dark grey mud	2900	0–3	3·2
Santa Monica Basin	Dark grey mud	2900	3–6	2·9
Tanner Basin	Light greenish-brown mud	5000	0·5–5	4·3
West Cortez Basin	Olive-brown mud	5700	0–4	3·9
West Cortez Basin	Olive-brown mud	5700	0–9	5·1
Santa Barbara Basin	Olive-brown mud, grey interbeds, finely laminated	1900	1–9	3·1
Bays				
Corpus Christi Bay (J)	Soft, grey, shelly mud	12	0–7	2·6
Corpus Christi Bay (J)	Grey plastic shelly mud	12	10–25	2·7
Corpus Christi Bay (J)	Grey firm creamy clay mud	12	25–35	2·6
Corpus Christi Bay (J)	Grey firm creamy clay mud	12	35–45	2·7
Corpus Christi Bay (J)	Grey soft plastic shelly mud	12	45–50	3·1
Corpus Christi Bay (J)	Grey plastic shelly mud	12	50–55	2·8
Corpus Christi Bay (J)	Grey plastic clay mud	12	55–60	3·8
Corpus Christi Bay (J)	Grey plastic clay mud	12	60–65	5·2
Corpus Christi Bay (H,K)	Grey mud	12	0–40	2·4
Galveston Bay	Grey plastic mud	9	20–30	3·5
Galveston Bay	Grey plastic clay mud	9	30–40	3·0
Galveston Bay	Grey plastic clay mud	9	40–50	2·7
Galveston Bay	Grey plastic clay mud	9	50–60	3·4
Gulf of Mexico				
Louisiana, Continental Shelf	Grey mud	40	0–8	5·5
Sabine Pass	Greyish brown mud	39	0–2	3·7

Table 1—(*contd.*)

Location	Description	Water depth (ft)	Depth in sediment (ft)	Ratio odd/even carbon-number
Fresh-water Lakes, Vilas County, Wisconsin				
North Trout Lake	Dark greenish-grey to black organic mud	4	0–2	4·0
South Trout Lake (core 2)	The same as above	58	0–5	4·7
South Trout Lake (core 2)	The same as above	58	5–10	5·3
South Trout Lake (core 3)	The same as above	58	0–3	4·7
South Trout Lake (core 3)	The same as above	58	3–8	4·6
South Trout Lake (core 3)	The same as above	58	8–12	4·6
Grassy Lake	Dark green to yellowish-brown organic mud	4	13–18	2·8
Grassy Lake	Yellowish-brown to black organic mud	4	18–23	3·6
Grassy Lake	Same as above	4	23–28	4·0
Grassy Lake	Same as above	4	28–33	4·6
Soils				
Lusk, Wyoming	Weathered from rocks of Tertiary age, rolling terrain		2–3	2·9
Sago Sumatra	Tropical soil, swampy		2–3	2·7
Saline Lake, San Bernardino Co., California				
Searles Lake	Parting mud between upper and lower salt body		61·8–62·5	3·8
Searles Lake	Same as above		65·8–66·5	3·5

Texas. These included the Mingus and Strawn shales of Pennsylvanian age and the Woodbine formation and Eagle Ford shale of Cretaceous age. Representative shale samples from a 1000 ft interval of fine-grained sediments of Pennsylvanian age were obtained from deep cores near the Scurry Reef in Scurry County, Texas. Cores of Woodbine shale from both above and below the producing zone in the East Texas field were also obtained.

Analytical Procedures and Data

Radiocarbon ages

Radiocarbon dating was used to verify the ages of the Recent sediment samples. The method of dating has been described by Burke and Meinschein (1955).

Extraction of hydrocarbons from sediments

The procedures used for extraction of the sediments have been described previously by Stevens *et al.* (1956) and also by Meinschein and Kenny (1957).

Table 2. Crude oils

Sample designation	Field	Reservoir formation	Age of reservoir formation	Depth (ft)	Ratio odd/even carbon-number
979	Chimire Field, Venezuela	L—2m	Oligocene	6363	1·08
819	West Cat Canyon, California	Sisquoc	Pliocene	3800	1·04
50	Capitan, California	Vaqueros	Miocene	1400	1·09
786	Gaiselberg, Austria	Tortonian	Miocene	7000	1·02
803	Belgian Anticl, California	Oceanic Zone	Oligocene	5530	1·13
1010	Guario, Venezuela	Naranja	Oligocene	5060	1·11
1201	Puchkirchen, Austria	Lattorfian	Oligocene	8100	1·10
832	Roosevelt, Utah	Green River	Eocene	9360	1·10
836	N. Duchesne, Utah	Green River	Eocene	8840	1·02
719	Pruitt, Texas	Olmos	Cretaceous	5000	0·95
781	Rough Range No. 1, Australia	Birdrong	Cretaceous	3610	1·06
697	Sylvestre, Venezuela	Fortuna	Cretaceous	9600	1·09
847	Tow Creek, Colorado	Mancos	Cretaceous	3800	1·03
1505	Walter Fair, Texas	Paluxy	Cretaceous	5400	0·91
1513	Ham Gossett, Texas	Woodbine	Cretaceous	3620	0·95
1517	Ham Gossett, Texas	Rodessa	Cretaceous	6220	0·95
1528	South Currie, Texas	Woodbine	Cretaceous	3000	0·91
1530	Ashby-Ramsey, Texas	Woodbine	Cretaceous	3200	0·92
1554	Grimes-Percilla, Texas	Woodbine	Cretaceous	5900	1·01
1555	Elkhart, Texas	Woodbine	Cretaceous	5800	0·99
1576	West Jacksonville, Texas	Rodessa	Cretaceous	8600	0·99
223	Lost Soldier, Wyoming	Morrison	Jurassic	1900	1·04
729	Omati No. 1, Papua (New Guinea)	—	Jurassic	13,700	1·08
864	North Premier, Saskatchewan	Shaunavon	Jurassic	3500	0·97
826	Rangley, Colorado	Shinarump	Triassic	4500	1·01
923	Virgin, Utah	Moenkopi	Triassic	500	0·99
343	Cross Roads, New Mexico	San Andres	Permian	4840	0·94
743	Dove Creek, Colorado	Hermosa	Pennsylvanian	6150	1·03
1113	Egmanton, England	Millstone Grit	Pennsylvanian	2100	1·05
1296	Kelly Snyder, Texas	Canyon	Pennsylvanian	6900	1·07
285	Garland, Wyoming	Madison	Mississippian	4200	1·02
351	Denton, New Mexico	"Miss. lime"	Mississippian	11,800	1·00
1145	Caddo, Oklahoma	Woodford	Mississippian	4400	1·06
29	Pegasus, Texas	"Dev. lime"	Devonian	11,900	1·00
361	Redwater, Alberta	D—3	Devonian	3200	1·03
25	Pegasus, Texas	Fusselman	Silurian	12,000	1·03
349	Brunson, New Mexico	Montoya	Ordovician	7800	1·03
1192	Willowdale, Kansas	Viola	Ordovician	4400	1·06
26	Pegasus, Texas	Ellenburger	Cambro-Ordovician	12,800	1·05
228	Lost Soldier, Wyoming	Deadwood	Cambrian	5150	0·99

The samples were air dried, and then extracted by a ball milling technique using as solvent a mixture of ten parts benzene and one part methanol. The solvent was subsequently removed from the organic extract by forced evaporation at 40°C. This step had the further effect of stabilizing the extract residues by removing the more volatile constituents in a reproducible manner retaining those *n*-paraffins having eighteen or more carbon atoms per molecule. The crude oils examined were also stabilized in a similar manner.

Isolation of n-*paraffins*

Enriched *n*-paraffin fractions were obtained by use of elution chromatography and in some instances by urea adduction. The methods and reagents used have been described by Evans *et al.* (1957). The stabilized residues of the crude oils and of the sediment extracts were dissolved in *n*-heptane and placed on activated silica

Table 3. Ancient sediments

Sample designation	Locality	Description	Formation	Age	Hydrocarbon content (wt. %)	Ratio odd/even carbon-number
Core 24, 5–8	Rifle, Colorado	Oil Shale	Green River	Eocene	0·60	2·3
		Marine Shales				
165, 1–9	Rusk Co., Texas	Grey shale, depth 3629–54 ft	Woodbine	Cretaceous	0·0045	1·49
165, 10–15	Rusk Co., Texas	Grey shale, depth 3658–86 ft	Woodbine	Cretaceous	0·0028	1·47
162, 3–2	Denton Co., Texas	Dark grey shale, depth 15–50 ft	L. Woodbine	Cretaceous	0·0021	1·39
162, 4–1	Dallas Co., Texas	Grey marl, depth 25–35 ft	Taylor	Cretaceous	0·0031	1·00
170, 79	Fergus Co., Montana	Black-grey shale, depth 20–30 ft	Colorado	Cretaceous	0·0043	1·79
170, 79	Fergus Co., Montana	Dark grey shale, depth 35–45 ft	Colorado	Cretaceous	0·0053	1·85
173, 32–38	Dallas Co., Texas	Dark grey fissile shale, depth 386–445 ft	Eagle Ford	Cretaceous	0·0025	2·2
173, 55	Dallas Co., Texas	Dark brown lignitic shale, depth 573–575 ft	Eagle Ford	Cretaceous	0·060	2·3
174, 10	Rusk Co., Texas	Dark grey shale, depth 3466 ft	Woodbine	Cretaceous	0·0020	1·32
174, 13–20	Rusk Co., Texas	Grey calcareous shale, depth 3471 ft	Woodbine	Cretaceous	0·0012	1·70
170, 85	Fergus Co., Montana	Greyish black shale, near surface	Morrison	Jurassic	0·0011	1·18
162, 1–1A	Palo Pinto Co., Texas	Grey shale, depth 17–22 ft	Strawn	Pennsylvanian	0·0062	1·04
162, 1–1B	Palo Pinto Co., Texas	Dark grey shale, depth 25–27 ft	Strawn	Pennsylvanian	0·0095	1·01
162, 1–1C	Palo Pinto Co., Texas	Grey brown shale, depth 32–40 ft	Strawn	Pennsylvanian	0·0055	1·03
162, 2–1	Palo Pinto Co., Texas	Grey shale, depth 23–30 ft	Strawn	Pennsylvanian	0·010	1·08
172, 1–2	Scurry Co., Texas	Black shale, depth 6851 ft	Canyon	Pennsylvanian	0·096	1·22
172, 1–2A	Scurry Co., Texas	Black shale, depth 6853 ft	Canyon	Pennsylvanian	0·090	1·22
172, 1–2B	Scurry Co., Texas	Black shale, depth 6856 ft	Canyon	Pennsylvanian	0·060	1·16
172, 3–4	Scurry Co., Texas	Black shale, depth 6859 ft	Canyon	Pennsylvanian	0·025	1·31
172, 3–4A	Scurry Co., Texas	Black shale, depth 6862 ft	Canyon	Pennsylvanian	0·020	1·22
173, 3–4B	Scurry Co., Texas	Dark grey shale, depth 6865 ft	Canyon	Pennsylvanian	0·018	1·26
172, 6–7	Scurry Co., Texas	Black shale, depth 6871 ft	Canyon	Pennsylvanian	0·014	1·56
172, 6–7A	Scurry Co., Texas	Dark grey shale, depth 6874 ft	Canyon	Pennsylvanian	0·013	1·20
172, 8	Scurry Co., Texas	Black fissile shale, depth 6876 ft	Canyon	Pennsylvanian	0·067	1·23
172, 9–10	Scurry Co., Texas	Black shale, depth 6880 ft	Canyon	Pennsylvanian	0·027	1·31
172, 12–13	Scurry Co., Texas	Black fissile shale, depth 6895 ft	Canyon	Pennsylvanian	0·024	1·34
172, 14–16	Scurry Co., Texas	Black fissile shale, depth 6913 ft	Canyon	Pennsylvanian	0·036	1·25
172, 22–24	Scurry Co., Texas	Black fissile shale, depth 6972 ft	Canyon	Pennsylvanian	0·13	1·16
172, 22–24A	Scurry Co., Texas	Black dense shale, depth 6987 ft	Canyon	Pennsylvanian	0·15	1·05
170, 27	Fergus Co., Montana	Grey sandy shale, near surface	Amsden	Pennsylvanian	0·013	1·11
170, 22	Fergus Co., Montana	Grey silty shale, near surface	Otter	Mississippian	0·039	1·44
170, 71	Fergus Co., Montana	Black shale, near surface	Tyler	Mississippian	0·0095	2·2
170. 64	Fergus Co., Montana	Black shale, near surface	Heath	Mississippian	0·0045	1·18
170, 43	Fergus Co., Montana	Black shale, near surface	Heath	Mississippian	0·027	1·03
146, 34	Cherokee Co., Oklahoma	Black shale, near surface	Chattanooga	Mississippian	0·15	0·99
188–B3	De Kalb Co., Tennessee	Dark brown shale, near surface	Chattanooga	Mississippian	0·20	1·00
1191	Kingman Co., Kansas	Dark grey shale, depth 4381 ft	Chattanooga	Mississippian	0·085	1·05
158, core 211	Carter Co., Oklahoma	Dark shale, near surface	Woodford	Mississippian	0·13	1·02
		Limestone				
172, 33	Scurry Co., Texas	Limestone, depth 7917 ft	Canyon	Pennsylvanian	0·30	0·98
170, 3	Fergus Co., Montana	Limestone, near surface	Heath	Mississippian	0·0080	1·15
170, 9, 10	Fergus Co., Montana	Black limestone, near surface	Heath	Mississippian	0·0045	1·00
170, 65	Fergus Co., Montana	Black limestone, near surface	Heath	Mississippian	0·0030	1·15

gel columns pre-wet with *n*-heptane. Additional aliquots of *n*-heptane were then passed through the columns. The resulting saturated hydrocarbon eluates were recovered by blowing away the eluent with filtered air at 40°C. Fractions enriched in *n*-paraffins were obtained by separation of these saturated hydrocarbons on alumina columns using alumina to sample ratios of approximately 10,000 to 1. *n*-Heptane followed by carbon tetrachloride was used as eluent. By use of these

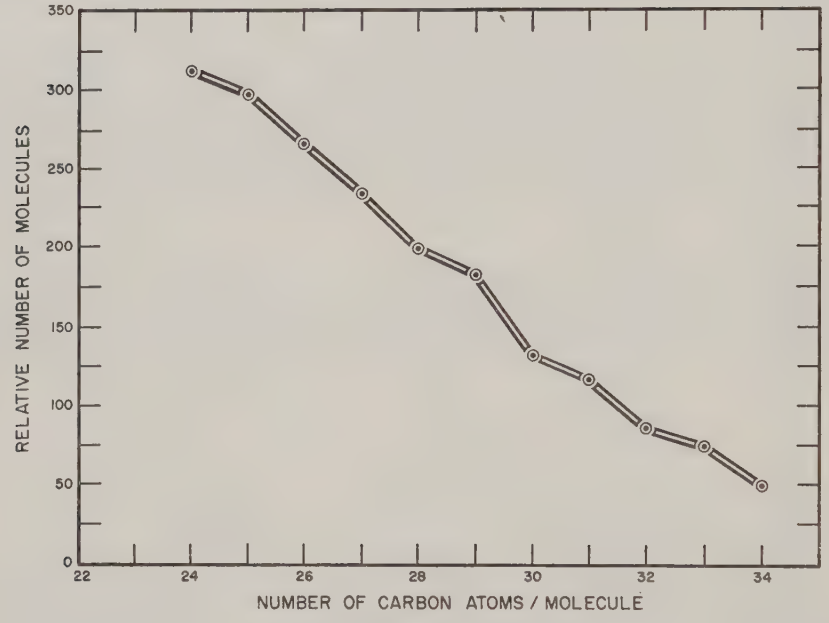

Fig. 1. Distribution of heavy *n*-paraffins recovered from a crude oil (Kelly-Snyder field, Scurry Co., Texas).

procedures, Evans *et al.* (1957) have separated naphthenes from alkanes. The carbon tetrachloride eluent was shown to recover nearly all the *n*-paraffins ranging in size from twenty-four to thirty carbon atoms per molecule.

Measurement of n-*paraffin distribution*

Distributions of the *n*-paraffins in the fractions were determined from mass spectra. These data were obtained with a Consolidated Electrodynamics Corporation model 21–103 mass spectrometer modified for use with high molecular weight compounds as described by O'Neal and Wier (1951). The mass spectral data were corrected to a monoisotopic basis for carbon and hydrogen, normalized to the major peak, and arranged in the grid form used by Clerc *et al.* (1955). The heavy *n*-paraffin parent peaks identified in this grid arrangement were calibrated using pure materials. Sensitivity and diffusion corrections obtained from the calibration data were used to adjust *n*-paraffin parent peak intensities to a relative molecular basis. These data give *n*-paraffin distributions such as the one shown for a crude oil in Fig. 1. Numerical values on the ordinate represent relative numbers of molecules. Numbers of carbon atoms per molecule are shown on the

abscissa. The graph shows an almost equal distribution between *n*-paraffin molecules containing odd and even numbers of carbon atoms. A very small prominence may be observed for *n*-paraffin molecules with 29 carbon atoms. Fig. 2 shows distributions obtained in a similar manner for heavy *n*-paraffins separated from extracts of a Recent sediment from a marine basin. A striking feature of this graph is the predominance of molecules having odd numbers of carbon atoms,

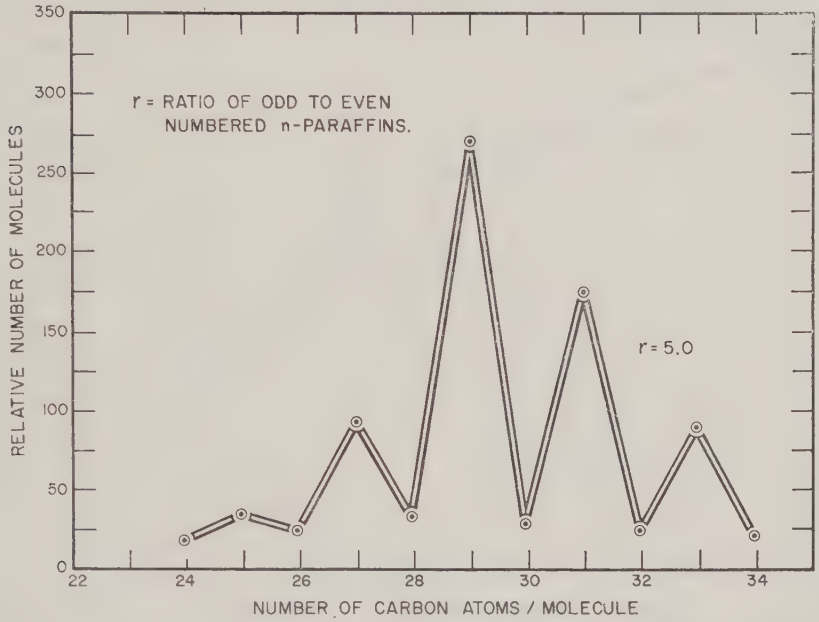

Fig. 2. Distribution of heavy *n*-paraffins recovered from a Recent sediment extract (Catalina Basin, 5–10 ft).

illustrated by the peaks at 25, 27, 29, 31 and 33. This predominance may be expressed numerically as a ratio obtained by dividing a summation of peak heights for the odd-carbon number *n*-paraffins by a similar summation of the even-carbon numbers. The value of such a ratio for the sample in Fig. 2 is 5·0. This ratio is the mean of two values computed by using different limits for the summations. One of these values was obtained by dividing the sum of corrected odd-carbon number *n*-paraffin peak heights at 25, 27, 29, 31 and 33 carbon atoms per molecule by the sum of the even-carbon number *n*-paraffins at 26, 28, 30, 32 and 34 carbon atoms per molecule. The other value was obtained by changing the denominator to include the even-carbon number *n*-paraffins at 24, 26, 28, 30 and 32 carbon atoms per molecule. The mean of these two ratios is used to avoid giving a bias to either even- or odd-carbon numbers. This bias could be caused by enhanced peak heights at the ends of the summation range.

Errors

Errors in the odd- to even-carbon-number ratios may arise from either instrumental sources or from impurities in the *n*-paraffin fractions. Changes in cracking

pattern and sensitivity in the mass spectrometer may cause variations in the *n*-paraffin parent peak sensitivities. However, these errors are largely cancelled when the *n*-paraffin distribution is expressed as an odd- to even-carbon-number ratio.

Larger errors may be caused by contamination of the *n*-paraffin fractions with materials such as heptacyclic naphthenes which contribute a background of ions

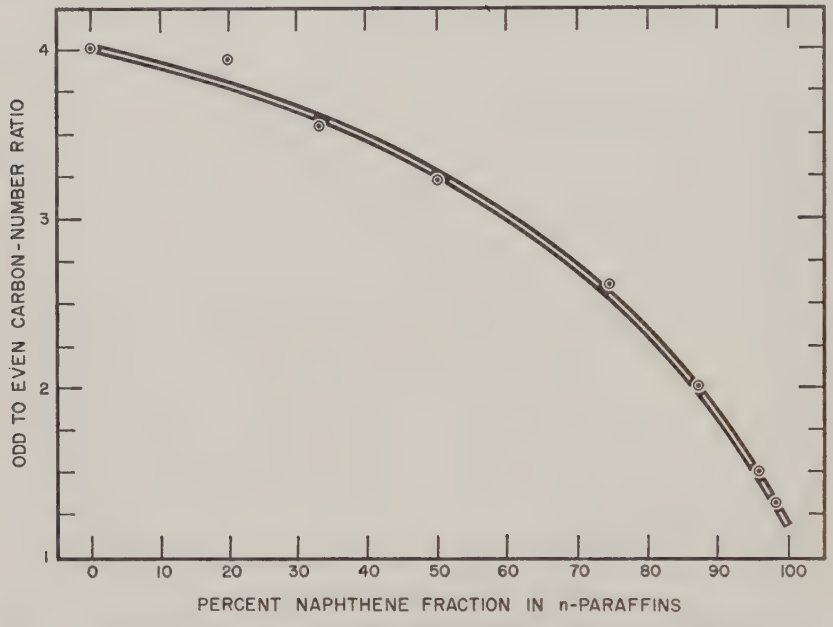

Fig. 3. Blends of naphthene fraction with Recent sediment *n*-paraffins.

to the mass positions of the *n*-paraffin parent peaks. Since these impurities add nearly the same values to both the numerator and denominator of the ratio, their contributions must be sizeable to change the values appreciably. Larger ratio values are subject to greater errors from this cause, since the background is a larger percentage of the denominator. Empirical tests were made to determine how much naphthene contamination could be tolerated in the *n*-paraffin fraction without seriously reducing the value of the odd- to even-carbon-number ratios. The curve of Fig. 3 shows the effects of naphthenic impurities on the odd- to even-carbon-number ratio for *n*-paraffins isolated by urea adduction from a Recent sediment extract. Naphthenes separated from a stabilized crude oil were added in varying amounts to the Recent sediment *n*-paraffins as shown on the abscissa of the curve in Fig. 3. The corresponding ratios obtained from the mixtures are shown on the ordinate. It may be seen from these data that naphthenic impurities up to 30 per cent of the fraction reduced the ratio by only 13 per cent of the difference between the ratio and 1·0. Mass spectrometric hydrocarbon analyses as reported by Clerc *et al.* (1955) were used to determine the amount of contamination in all the *n*-paraffin fractions examined. Although these analyses give only

approximate data, they provide a useful empirical guide to the amount of impurities permissible in the *n*-paraffin fractions. By means of this screening procedure fractions containing naphthenes in concentrations of the order of 30 per cent or more were either further purified or discarded.

Discussion and Results

The identification of source beds may be complicated by prior loss of large portions of oil from the rock, leaving behind the organic debris and hydrocarbon

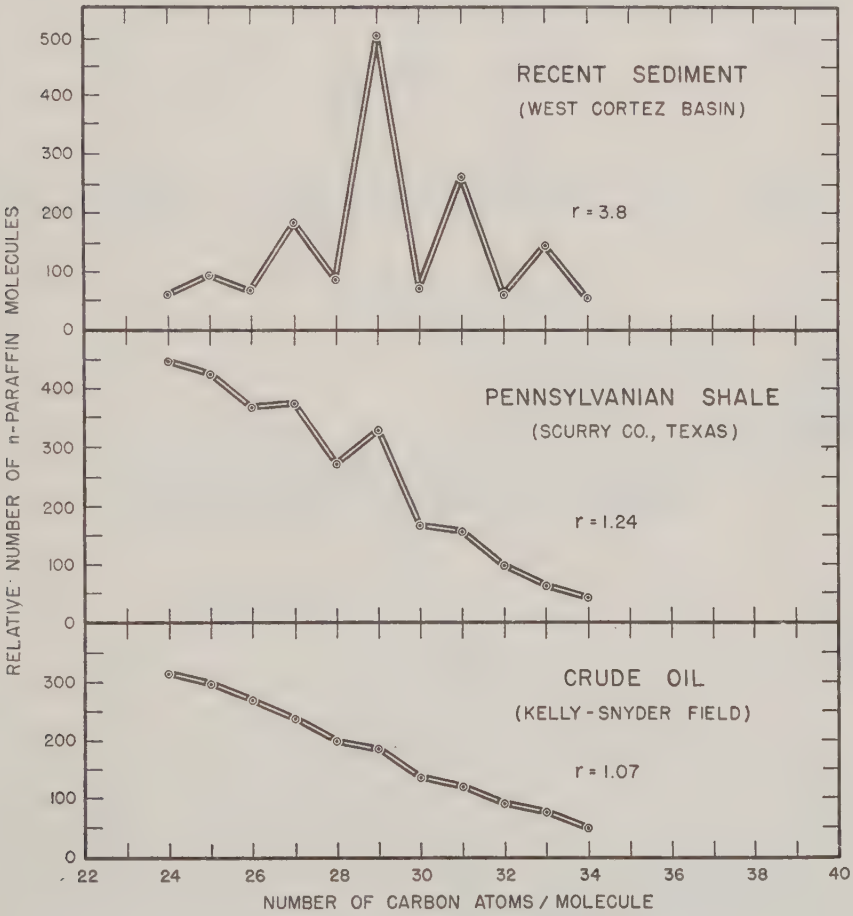

Fig. 4. *n*-Paraffin distributions for a Recent sediment, a marine shale and a crude oil.

residue possibly weighted with the heavier, less volatile constituents of the oil. These heavy, oily constituents, including *n*-paraffins, may provide clues to the recognition of source beds since they are a part of both the residue in the rock and the oil.

Examples of heavy *n*-paraffin distributions, expressed numerically by ratios of odd- to even-carbon-numbered molecules, are shown in Fig. 4. These examples

include a Recent sediment from a marine basin, a core of ancient marine shale, and a crude oil with ratios of 3·8, 1·24 and 1·07 respectively. The Recent sediment shows increasing abundance of odd-numbered carbon molecules with size, up to the maximum at 29 carbon atoms. In contrast, the shale extract and the crude oil show a decreasing abundance with size. The example for the crude oil is consistent with data reported previously (Stevens *et al.* 1956; Evans *et al.* 1957), showing almost no preference for molecules with odd numbers of carbon atoms.

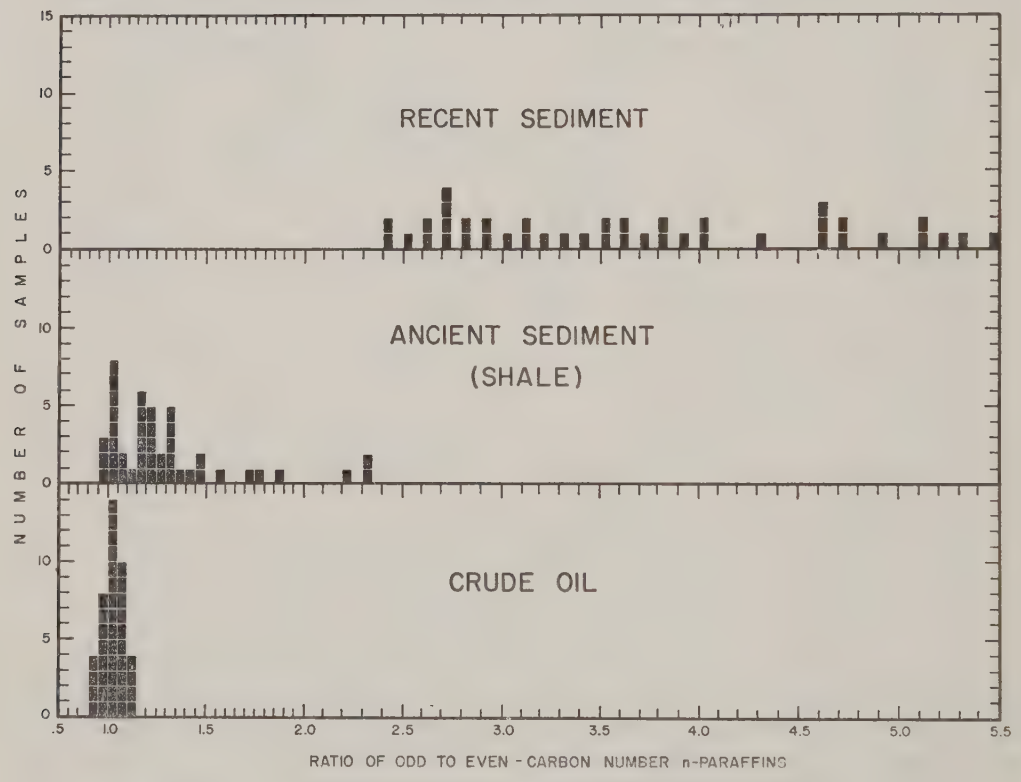

Fig. 5. *n*-Paraffin distributions in crude oils and sediment extracts.

The distribution of odd- to even-carbon-number ratios for *n*-paraffins in a variety of crude oils is shown at the bottom of Fig. 5. The values for 39 representative examples cluster within narrow limits near a value of 1·0, indicating that crude oils in general contain heavy *n*-paraffins which are almost equally distributed between molecules containing even and odd numbers of carbon atoms. The odd- to even-carbon-number ratios for all the Recent sediments examined are also shown in Fig. 5. These ratios are distributed rather uniformly in the range 2·4 to 5·5, indicating that a preference for heavy *n*-paraffins with odd-numbers of carbon atoms is widespread in Recent sediments. The range of values is significantly greater than for crude oils. In the centre of Fig. 5 is shown the distribution of odd- to even-carbon-number ratios for *n*-paraffins extracted from ancient sediments including a variety of shales and some limestones. The ratios, in general, are

lower than those of Recent sediments. Some values are close to 1·0 which has been shown to be characteristic of the n-paraffins in crude oils.

The assumption is often made that hydrocarbons originally deposited with sediments of past geologic ages were similar to those in Recent sediments of today. If this is true, the n-paraffin distributions in nearly all of the ancient shales and limestones examined have changed since the time of deposition. The smaller ratios of odd- to even-carbon-number n-paraffins found in most of the rocks appear consistent with the addition of petroleum-like hydrocarbons, either by migration

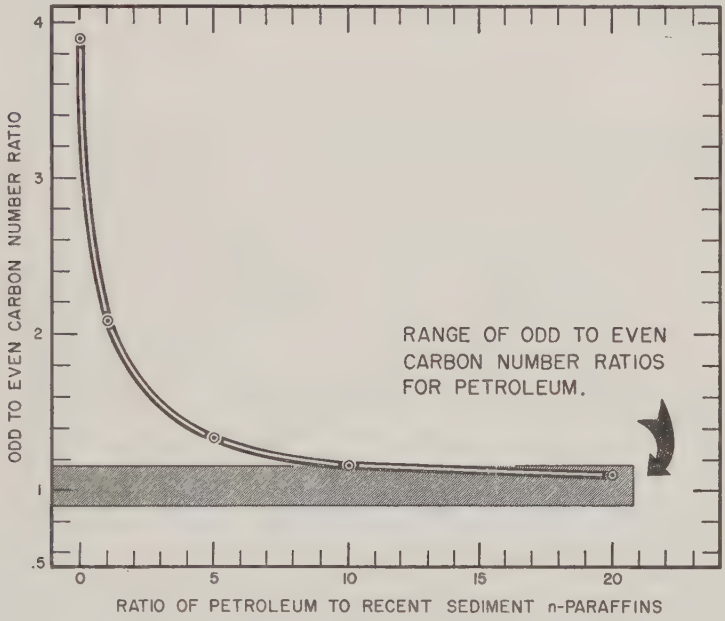

Fig. 6. Odd-to-even carbon-number ratios for mixtures of petroleum and Recent sediment n-paraffins.

from other sediments or by generation in place. These petroleum hydrocarbons contribute n-paraffins, diluting the original mixture, and changing the distribution to give the smaller odd- to even-carbon-number ratios observed. This reduction in ratio is illustrated in Fig. 6, which shows the results of diluting n-paraffins from Recent sediment with those isolated from a crude oil. The Recent sediment n-paraffin had an original odd- to even-carbon-number ratio of 3·9 as shown on the ordinate of Fig. 6. Progressively greater dilutions as shown on the abscissa, caused the ratio to decrease rapidly at first and to finally become diluted to near the values for petroleum after addition of petroleum n-paraffins approximating ten times the amount of sediment n-paraffin. This extinction of the odd-carbon preference by dilution may be useful in the recognition of source beds.

"Source beds", as defined in the A.G.I. Glossary (Howell, 1957), are rocks in which oil or gas has been generated. Although the occurrence of source beds as defined is debatable, we shall assume their existence as a working hypothesis. Beds fitting this definition should contain a mixture of heavy n-paraffins, similar

to petroleum which has obscured the predominance of odd-carbon numbered n-paraffins, assumed to have been present in the sediment at the time of deposition. Regardless of the level of predominance of odd-carbon sizes in the original sediment, the shales and limestones which now have n-paraffins exhibiting ratios significantly greater than those for crude oils have not generated enough hydrocarbons to form a petroleum-like mixture (Fig. 5). This criterion could narrow the search for source beds by a process of elimination. Although the selection of ancient sediment

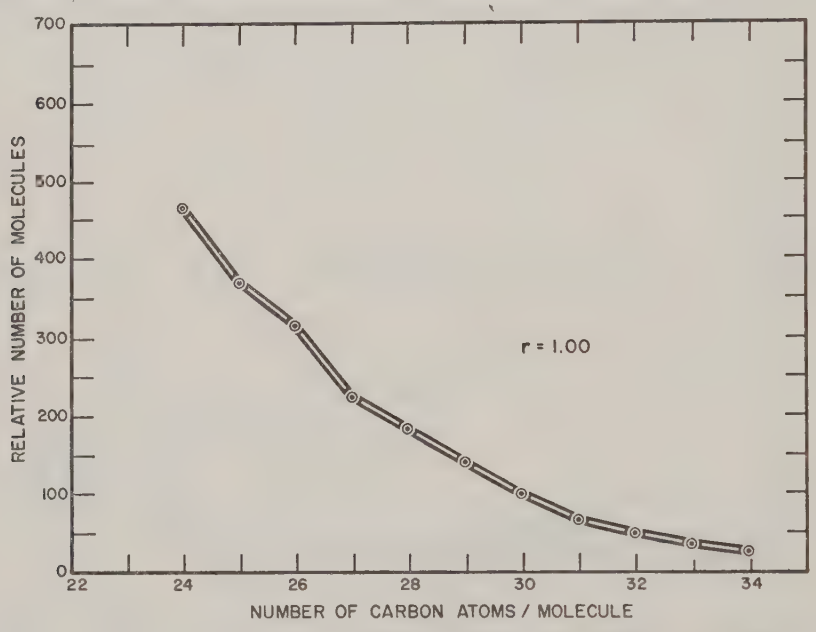

Fig. 7. Distribution of heavy n-paraffins recovered from Chattanooga shale (De Kalb County, Tennessee).

samples was biased to include possible source rocks, 65 per cent of those examined had n-paraffin odd–even carbon number ratios differing from petroleum (Table 3).

A number of the shales and limestones studied are distinctive in that they have n-paraffin odd- to even-carbon-number ratios similar to those for petroleum (Fig. 5). These examples include, among others, postulated "source beds" such as the Chattanooga, Woodford and Heath shales. The distribution of heavy n-paraffins obtained from a sample of Chattanooga shale is shown in Fig. 7. The shales bearing petroleum mixtures are not restricted to those containing large quantities of hydrocarbons. There are numerous examples of shales with low hydrocarbon content which exhibit petroleum-like distributions of heavy n-paraffins (Table 3). In these instances, the sediments have either yielded their hydrocarbons or were very low in hydrocarbon content in the beginning.

Conclusions

The results of this study may be summarized as follows:

(1) Predominance of heavy n-paraffins with odd numbers of carbon atoms per molecule is widespread in Recent sediments.

(2) Crude oils in general contain heavy n-paraffins which are almost evenly distributed between molecules of odd and even numbers of carbon atoms.

(3) Postulated source beds analysed in this study are distinctive in that they contain heavy n-paraffins which are almost equally distributed between molecules of odd and even numbers of carbon atoms as in petroleum. It should be apparent, of course, that this ratio alone cannot be used to distinguish a source bed from a bed into which oil has migrated.

(4) Most of the shales and limestones examined contain n-paraffins with odd- to even-carbon-number ratios significantly greater than that for crude oil. These rocks are regarded as not having generated enough hydrocarbon to become "source beds".

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Some chemical aspects of petroleum genesis as related to the problem of source bed recognition

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Introduction

Source sediments of petroleum are, by definition, rocks in which appreciable quantities of crude oil have been generated. It is recognized that the composition of crude oil varies widely. As a criterion for genesis, however, it is considered that the following characteristic fractions must be present and in appreciable quantity:

(a) The light aromatic hydrocarbons consisting of benzene, toluene, ethylbenzene, the xylenes, naphthalenes, etc.

(b) The light aliphatic hydrocarbons consisting of methane, ethane, propane, the butanes, pentanes, etc.

(c) The intermediate and heavy aliphatic, naphthenic, and aromatic hydrocarbons.

(d) The asphaltic constituents, commonly referred to as resins, maltenes and asphaltenes. These compounds consist of a large proportion of high molecular weight, non-hydrocarbon material. Elements other than carbon and hydrogen are primarily oxygen, nitrogen and sulphur.

Recognition of source sediments of petroleum is complicated by the fact that a portion—possibly even a very large portion—of the oil generated therein has been expelled during compaction and lithification of the sediment. Crude oil as it leaves the source sediment is never the sole product of organic diagenesis. Further, certain properties of the oil may be altered during migration and accumulation. Nevertheless, the oil in the reservoir and the residual organic material in the source sediment are products of a common genesis process; and a definite relationship must exist between them.

Methods for recognition must necessarily be based upon observed characteristics of rocks which are believed to have yielded petroleum in quantity, as opposed to those believed never to have yielded oil. Many techniques have been used: micropaleontological, mineralogical and chemical. Since all gradations between prolific source sediments and totally non-oil producing rocks almost certainly exist in nature, it is thought that quantitative statements with respect to source sediments can come only with understanding of their formation.

In this paper the origin as related to environment of the above major constituents of petroleum and their distribution in ancient carbonaceous rocks will be discussed. The discussion will draw on data both from the literature and from researches presently in progress on the Gulf Fellowship at Mellon Institute.

The Low Molecular Weight Aromatic Hydrocarbons

Low molecular weight aromatic hydrocarbons are defined for the purpose of this study as benzene and naphthalene and their alkyl-substituted derivatives

boiling up to perhaps 250°C under atmospheric pressure. Expressed another way, these compounds make up a portion of the naphtha and light fuel oil fractions of crude oils.

The low molecular weight aromatic hydrocarbons comprise up to 5 per cent or more of the total hydrocarbon fraction of crude oils and are considered one of its most characteristic hydrocarbon constituents. Their distribution, however, in other natural bitumens, such as oil shale, coals, and even marine shales and limestones believed to be source rocks of petroleum, has received little attention.

From the viewpoint of genesis, the aromatic hydrocarbons are of particular interest in that the lower molecular weight members are not recognized as products of living organisms. Examples are benzene, toluene, ethylbenzene and the xylenes. Even those recognized as natural products are not too widely distributed. The presence of cymene is reported in several essential oils (Jones and Lahen, 1943; Anon., 1944; Fujita, 1950; Penfold and Morrison, 1951); naphthalene in oak moss (Stoll and Scherrer, 1937) (*Evernia prunastri*); and naphthalene, methyl naphthalene and dimethyl naphthalenes in rice embryo oil (Sebe, 1943). In some instances it is questionable whether the compounds actually are present in the organisms or are formed during the preparation of the extracts. No reports of their presence in animals, lower plants, bacteria and particularly aquatic organisms, have been found. Similarly, no references have been found concerning their formation during autolysis or bacterial decomposition of plant and animal material. Despite their paucity in living organisms, no systematic effort has been made to determine at what time these interesting compounds are formed during the genesis of the source rock and to what extent the initial environment affects their ultimate abundance in the rock.

To investigate the distribution and origin of the low molecular weight aromatic hydrocarbons in both ancient and recent sediments, it was necessary to develop a special analytical procedure (Erdman *et al.*, 1958a). The range of the procedure extends from the parent compound, benzene, through compounds containing as many as ten alkyl carbons attached to the ring. In the naphthalene series, the range is from naphthalene to naphthalenes with four alkyl carbons attached. Owing to the fact that the procedure determines the number of aromatic rings, concentrations are reported in terms of phenyl (benzenoid) and naphthyl (naphthalenic) rings. Under most conditions, the method is capable of detecting less than 0·1 p.p.m. of phenyl rings and 0·01 p.p.m. of napthyl rings, based on the dry weight of the rock sample. For an oil containing 3 per cent of low molecular weight aromatic hydrocarbons, these limits would represent the equivalent of less than 3 mg of oil per kilogram of rock.

The first objective was to investigate the distribution of low molecular weight aromatic hydrocarbons in a variety of ancient carbonaceous rocks. Particular attention was given to obtaining rocks which were almost certainly sources of commercial quantities of crude oil. Other carbonaceous rocks were marine sections which apparently had not yielded oil and non-marine sections including coals and oil shale.

In Fig. 1 are shown the locations with respect to the electric log of six cores cut from marine Oligocene shales in south-east Texas. The upper Anahuac shale is

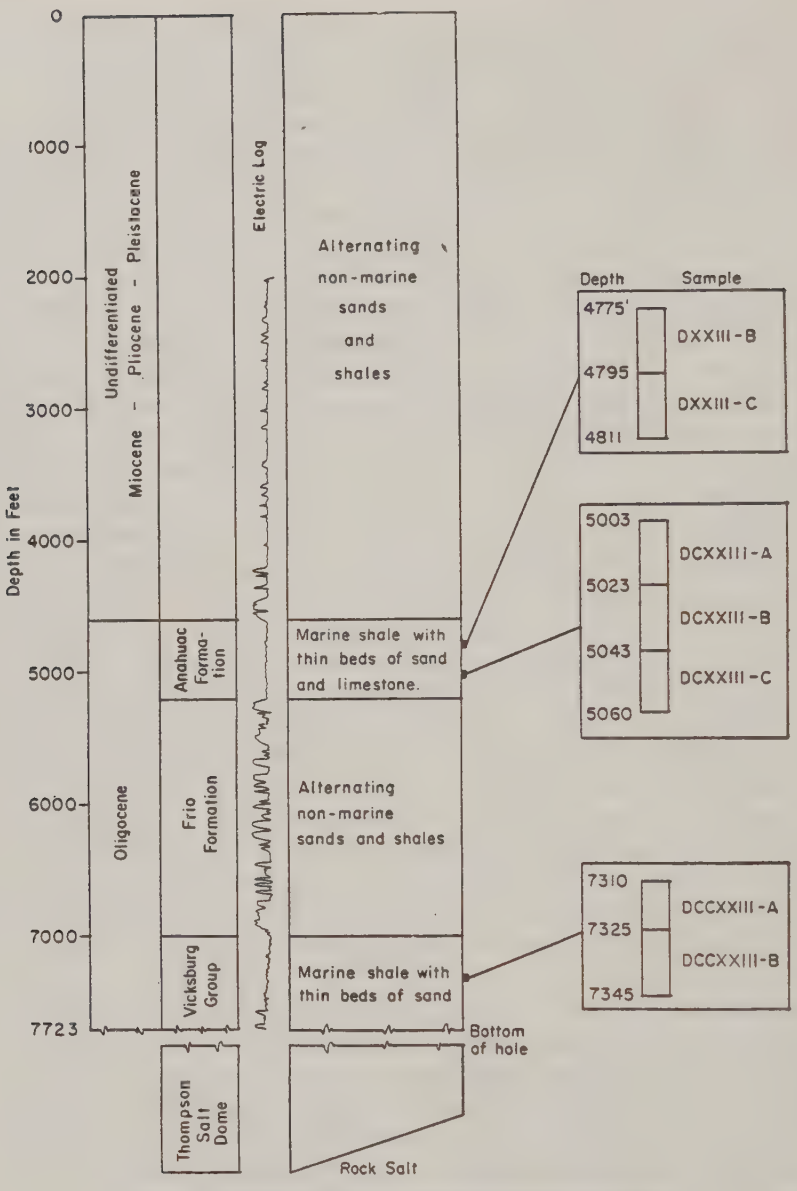


Fig. 1. Location of ancient marine sediment samples from Anahuac and Vicksburg formations.

believed to be the principal source of the oil in the Miocene sand above; the lower Anahuac shale, of the oil in the Frio sand below; and the Vicksburg shale, of the oil in the adjacent Vicksburg sand. The analytical results are shown in Table 1. The term "trace" here indicates that the aromatic hydrocarbon ring system was detected but that the concentrations were very low, particularly for the Anahuac. The fact that the Vicksburg shale is richer in aromatics, both in absolute amount

and in proportion to the total organic carbon content, is interesting when it is considered that this rock is under a greater overburden than the Anahuac.

In Table 2 are provided similar data for Cretaceous marine limestones from Venezuela. The La Luna limestone is closely associated with the Mara production and may be both a source and reservoir rock. The Querecual samples taken from three different wells, at least as yet, have not been associated with crude oil deposits. Again it will be noted that aromatic hydrocarbons are present in small amounts in all these samples.

Table 1. Occurrence of low molecular weight aromatic hydrocarbons in marine Oligocene shales

Sample designation	Geologic formation	Carbon content (%)		Weight of aromatic hydrocarbon rings (p.p.m.)	
		Total organic	Carbonate	Phenyl (C_6H_5)	Naphthyl ($C_{10}H_7$)
DXXIII-B	Upper Anahuac (4775–4795 ft)	0·16	0·96	trace trace	trace trace
DXXIII-C	Upper Anahuac (4795–4811 ft)	0·25	0·53	trace trace	trace trace
DCXXIII-B	Lower Anahuac (5023–5043 ft)	0·27	1·49	trace trace	trace trace
DCXXII-C	Lower Anahuac (5043–5060 ft)	0·21	0·99	trace 0·1	trace trace
DCCXXIII-A	Vicksburg (7310–7325 ft)	0·51	0·56	5·2 6·3	0·02 0·04
DCCXXIII-B	Vicksburg (7325–7345 ft)	0·42	0·77	4·9 4·3	0·03 0·03

In Table 3 are provided data for samples obtained from a core cut by the Army Corps of Engineers in south-west Pennsylvania. These sections probably range from marine to fresh-water deposits. Again, it will be noted that aromatic hydrocarbons are present in all these samples, including the coal from the Pittsburgh seam.

Finally, in Table 4 are provided data for three more coals from Pennsylvania and for a sample of Green River oil shale from Colorado. While crude oil apparently has been generated in certain parts of the Green River series, the oil shale is not looked upon generally as a typical source of petroleum.

These data show clearly that low molecular weight aromatic hydrocarbons are widely distributed in ancient rocks. Indeed, some of the highest absolute concentrations are recorded for rocks which are not thought to be source beds.

The genesis of low molecular weight aromatic hydrocarbons in almost all organic-rich rocks is not surprising. Further, in the case of source rocks, the

expulsion of oil would tend to deplete the store of the aromatic hydrocarbons more rapidly than the total organic content. Nevertheless, re-examination of the data expressing the aromatics as a proportion of the total organic carbon content, as shown in Table 5, does indicate a generally higher yield of aromatics in those rocks believed to be source beds.

Table 2. Occurrence of low molecular weight aromatic hydrocarbons in marine Cretaceous limestones

Sample designation	Geologic formation and basin	Carbon content (%)		Weight of aromatic hydrocarbon rings (p.p.m.)	
		Total organic	Carbonate	Phenyl (C_6H_5)	Naphthyl ($C_{10}H_7$)
DXXIX-A	La Luna Maracaibo (8281–8314 ft)	2·24	8·37	23·0 19·0	0·18 0·22
DXXXIII-A	Querecual E. Venezuela Sta Barbara area (2096–2116 ft)	0·59	11·02	0·2	trace
DCXXXIII-A	Querecual E. Venezuela Sta Barbara area (2585–2595 ft)	0·26	11·44	0·1	trace
DXXXVII-A	Querecual E. Venezuela Sta Barbara area (3597–3609 ft)	1·11	0·89	trace	trace
DXXXVIII-A	Querecual E. Venezuela Sta Barbara area (10,893–10,910 ft)	1·88	0·35	3·8	0·02

The second phase of the study was to ascertain when, and under what conditions, the low molecular weight aromatic hydrocarbons make their appearance in sediments, and which environmental conditions seemed to be the most favourable. Accordingly, samples for study were collected from four typical present-day aquatic environments. Sampling was conducted at four locations in each environment in order to permit an evaluation of local variations. Sampling was from a zone sufficiently deep within the sediment to be below the zone of major bacterial activity and below the possibility of contamination through the activities of man.

General descriptive information concerning the character and composition of the sediments from these four environments is provided in Tables 6 through 9. Age

of the sediments from one location in each environment was obtained by C^{14} dating. Trends in pH, carbonate content and total organic carbon content show that the samples do, in fact, span environmental conditions from semi-marine to fresh-water swamp.

Examination of all these samples failed to reveal the presence of low molecular weight aromatic hydrocarbons at concentrations within the limits of the analytical

Table 3. Occurrence of low molecular weight aromatic hydrocarbons in a Pennsylvanian depositional sequence

Sample designation	Geologic formation	Organic carbon content (%)	Weight of aromatic hydrocarbon rings (p.p.m.)	
			Phenyl (C_6H_5)	Naphthyl ($C_{10}H_7$)
DXXXI-A	Monongahela, carbonaceous clay shale; second major unit above the Pittsburgh coal (32·9–33·55 ft)	10·8	10·3	0·07
DXXXI-B	Monongahela, silty shale; first major unit above the Pittsburgh coal (40·8–41·4 ft)	1·59	2·0	0·02
DCXXXI-A	Monongahela, bituminous coal; Pittsburgh (50·15–50·85 ft)	68·0	0·2	0·02
DCCXXXI-A	Conemaugh, limestone; immediately beneath the Pittsburgh coal (55·2–55·85 ft)	0·50	0·5	0·01
DCCXXXI-B	Conemaugh, clay shale; beneath the Pittsburgh coal (60·8–61·5 ft)	5·89	9·2	0·37

method. Assuming that the aromatics were present just below the detection limit and that none were lost during lithification, these sediments could not yield more than 3 mg of a typical crude oil per kilogram dry weight of sediment. Alternately expressed on a carbon ratio basis, these limiting concentrations, as provided in Tables 10 and 11, show that the recent sediments are much leaner than their likely ancient equivalents.

The above data (Erdman, 1958b) for both recent and ancient sediments show that a chemical mechanism for the genesis of varying quantities of low molecular weight aromatic hydrocarbons must take place in aquatic sediments after life processes have ended. On the basis of current knowledge of the composition of the

Table 4. Occurrence of low molecular weight aromatic hydrocarbons in Pennsylvanian coal samples and an Eocene oil shale

Sample designation	Geologic formation	Carbon content (%)		Weight of aromatic hydrocarbon rings (p.p.m.)	
		Total organic	Carbonate	Phenyl (C_6H_5)	Naphthyl ($C_{10}H_7$)
DXXXIV-A	Allegheny, cannel (pseudo) coal; Upper Freeport, Oakmont mine	79·9	0·02	trace	0·03
				trace	0·03
DXXXVI-A	Allegheny, bituminous coal; Upper Freeport, Oakmont mine	56·4	0·01	2·6	0·02
				2·2	0·01
DXXXV-A	Allegheny, bituminous coal; Lower Freeport, Sekora strip mine	77·0	0·04	1·8	0·03
				1·9	0·02
DXXXII-B	Green River, oil shale; 13–14 ft below Mahogany marker	29·0	2·92	29·3	0·28
				27·1	0·12

Table 5. Proportion of the total organic carbon content of ancient marine and non-marine rocks represented by low molecular weight aromatic ring carbon

	Ratio of arom. ring C to total org. C $\times 10^4$		
Ancient marine		Ancient non-marine	
Oligocene shales	~0·6	~0·001	Pennsylvanian coals
	~0·4	0·04	
	~0·4	0·02	
	~0·5	0·003	
	10·6		
	10·6	0·92	Eocene oil shale
Cretaceous limestone	8·8		
	1·9		
	0·3		
	0·4		
spread	0·3–10·6	0·001–0·92	spread

Table 6. Recent semi-marine sediments

Sample designation	Description	pH of core liquid	Carbon content (%)	
			Total organic	Carbonate
CCCX-B	silty clay; depths 120–135 cm			
Loc. 1		8·1	0·85	0·32
Loc. 2		8·3	0·57	0·53
Loc. 3A	age 3480 ± 140 years	8·2	0·53	0·71
Loc. 4		8·2	0·55	0·57

Table 7. Recent sound or lagoonal sediments

Sample designation	Description	pH of core liquid	Carbon content (%)	
			Total organic	Carbonate
CCCXVII-A	silty clay; depths 120–135 cm			
Loc. 1		8·3	1·32	0·065
Loc. 2		8·3	0·57	0·10
Loc. 3	age 1400 ± 100 years	8·2	1·48	0·12
Loc. 4		8·2	0·80	0·025

Table 8. Recent coastal brackish marsh sediments

Sample designation	Description	pH of core liquid	Carbon content (%)	
			Total organic	Carbonate
CCCXVIII-B	silty clay			
Loc. 1	depth 130–145 cm	7·8	2·79	<0·01
Loc. 2D	depth 125–140 cm	8·2	1·98	<0·01
Loc. 3	depth 125–140 cm	7·9	2·17	<0·01
Loc. 4	depth 125–140 cm; age 2220 ± 170 years	7·9	5·79	0·01

Table 9. Recent fresh-water swamp sediments

Sample designation	Description	pH of core liquid	Carbon content (%)	
			Total organic	Carbonate
CCCXXVII-B	peaty; depths 115–130 cm			
Loc. 1	age 2820 ± 250 years	6·1	48·1	<0·05
Loc. 2		6·2	50·0	<0·05
Loc. 3		6·3	47·0	<0·05
Loc. 4		6·1	47·7	<0·05

Table 10. Comparison of ancient marine rocks with related recent sediments with respect to the proportion of organic carbon represented by low molecular weight aromatic ring carbon

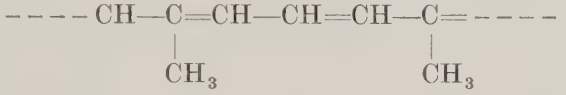
Ancient		Recent	
	Ratio of arom. ring C to total org. C $\times 10^4$	Maximum possible value for the ratio of arom. ring C to total org. C $\times 10^4$	
Oligocene marine shales			near-shore marine
	~0·6	0·12	
	~0·4	0·18	
	~0·4	0·19	
	~0·5	0·19	
	10·6		
	10·6		sound
		0·08	
Cretaceous marine limestones		0·18	
	8·8	0·07	
	1·9	0·13	
	0·3		
	0·4		

Table 11. Comparison of ancient non-marine rocks with related recent sediments with respect to the proportion of organic carbon represented by low molecular weight aromatic ring carbon

Ancient		Recent	
	Ratio of arom. ring C to total org. C $\times 10^4$	Maximum possible value for the ratio of arom. ring C to total org. C $\times 10^4$	
Pennsylvanian coals			coastal brackish marsh
cannel (pseudo)	0·001	0·04	
		0·05	
bituminous	0·04	0·05	
	0·02	0·018	
	0·003		
			northern fresh-water swamp
Eocene oil shale		0·002	
	0·92	0·002	
		0·002	
		0·002	

organic fraction of recent sediments and the type of chemical reactions which might take place under earth conditions, several groups of compounds stand out as probable precursors.

The first group is the conjugated unsaturates, of which squalene, the carotenes and xanthophylls are examples. These compounds are characterized by a conjugated chain with branch methyls, i.e.



and are formed in considerable quantities by both terrestrial and aquatic plants and animals. In fact, the typical yellow-to-brown colour of marine algae, such as

Table 12. Residues of amino acids in Oligocene marine shales and an Eocene oil shale

	Nitrogen (%)		α-amino N / total N ratio × 100
	Total reduced	α-Amino	
Anahuac shale—Upper:			
DXXIII-B	0·022	—	—
DXXIII-C	0·035	0·00007	0·2
Anahuac shale—Lower:			
DCXXIII-B	0·032	—	—
DCXXIII-C	0·034	0·00014	0·4
Vicksburg shale:			
DCCXXIII-A	0·052	0·00021	0·4
DCCXXIII-B	0·049	—	—
La Luna limestone:			
DXXIX-A	0·126	0·00020	0·2
Green River shale:			
DXXXII-A	0·947	0·0021	0·2

diatoms, the laminaria or kelps, sargassum and the other fucoid seaweeds are due largely to a xanthophyll, known as fucoxanthin. Isolated in a crude form, this oxygen-containing, tacky, brown material may easily be mistaken for the asphaltic fraction of crude oil, although in chemical structure little similarity exists.

Fox and collaborators (Fox, 1937, 1944; Fox and Anderson, 1941; Fox *et al.*, 1944) have shown that these conjugated unsaturated compounds survive into marine sediments for many thousands of years. They do not, however, survive through geologic time. Under mild thermal conditions these compounds are reported to yield up to several per cent aromatic hydrocarbons. Accordingly, *m*-xylene was obtained from bixin by Van Hasselt (1911) and from capsanthin

by Zechmeister and Cholnoky (1930); while toluene, *m*-xylene, and 2:6-dimethylnaphthalene were obtained from other carotenoids by Kuhn and Winterstein (1932, 1933a, b). Jones and Sharpe (1948) confirmed the formation of 2:6-dimethylnaphthalene from carotene. In these studies the solids were thermally decomposed, and no mention is made of the chemical fate of the bulk of the material apparently not converted to the aromatics.

Table 13. α-Amino acid content of recent sediment samples

Sample designation	Total organic carbon (%)	Total reduced nitrogen (%)	$\frac{\text{α-amino N}}{\text{total N}}$ ratio × 100	$\frac{\text{Est. α-amino C}}{\text{total organic C}}$ ratio × 100
CCCX-B				
Loc. 1	0·85	0·086	6·5	2·5
Loc. 2	0·57	0·048	8·5	2·7
Loc. 3A	0·53	0·044	9·7	3·0
Loc. 4	0·55	0·050	7·4	2·5
CCCXVII-A				
Loc. 1	1·32	0·128	8·3	3·0
Loc. 2	0·57	0·062	7·3	2·9
Loc. 3	1·48	0·173	6·6	2·9
Loc. 4	0·80	0·082	5·1	2·0
CCCXVIII-B				
Loc. 1	2·79	0·155	24·5	5·1
Loc. 2D	1·98	0·104	19·2	3·8
Loc. 3	2·17	0·122	16·4	3·4
Loc. 4	5·79	0·292	24·3	4·6
CCCXXVII-B				
Loc. 1	48·1	2·08	49	7·9
Loc. 2	50·0	2·29	49	8·4
Loc. 3	47·0	2·48	47	9·2
Loc. 4	47·7	2·02	51	8·1

The degradation of carotene has been repeated in this laboratory, this time in dilute solution. Reaction in solution more closely duplicates conditions in the earth, since under natural conditions the carotenoid material would be highly dispersed in the organic matrix. In addition, intra- rather than inter-molecular re-arrangements are favoured because of separation of the reacting molecules. The reaction was found to proceed rapidly at 170°C, more slowly at 150°C, and at a slow but finite rate at even 119°C. At the highest temperature, toluene, *m*-xylene, 2:6-dimethylnaphthalene and possibly 2:5-dimethylnaphthalene were recognized among the volatile products. The manner in which these compounds can be formed from the carotene molecule is shown in Fig. 2. The remainder of the material was converted to a near colourless oil. While the analysis is not yet complete, it is believed to consist of naphthenic and aromatic rings with attached

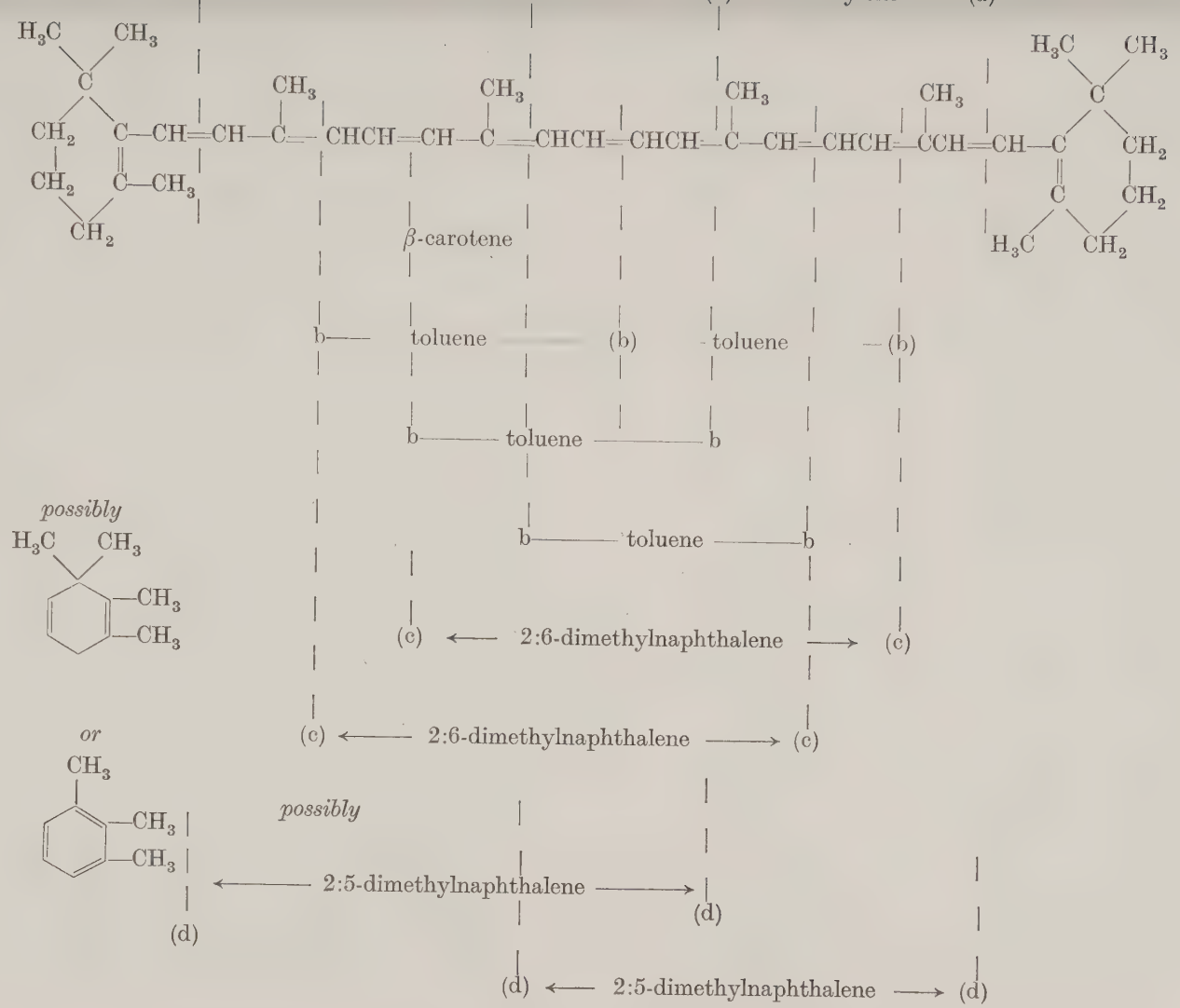
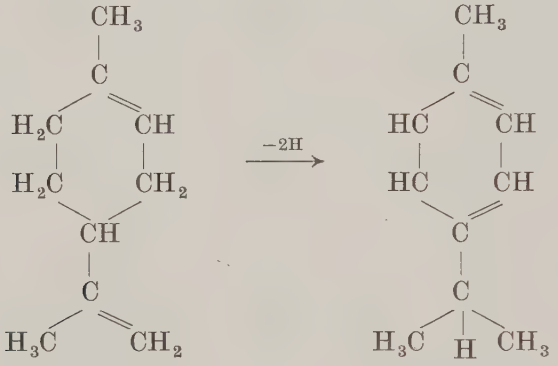


Fig. 2. Ways in which β-carotene may degrade to give cyclic compounds.

hydrocarbon chains of varying length. These studies are being continued to include the degradation of related compounds, particularly fucoxanthin.

The second group of compounds to be considered as possible precursors of the low molecular weight aromatic hydrocarbons is the terpenes. These compounds are widely distributed in woody plants and have been shown to be produced by some algae, such as kelps (Sirahama, 1938). In a sense, the terpenes might be considered as derivatives of the polyene pigments, the cyclization taking place in the living organism. Thus, in its simplest cases only dehydrogenation and rearrangement of bonds would be needed to yield aromatic hydrocarbons:



limonene *p*-cymene

At present little is known about the distribution of the terpenes in micro-aquatic organisms which make up the great organic productivity of the sea, and even less concerning their fate after the death of the organism and deposition.

The third group of compounds to be considered as possible precursors of the low molecular weight aromatic hydrocarbons is the highly unsaturated fatty acids common to many forms of aquatic life. For example, Klenk (1958) reports that in the fish oils the most highly unsaturated polyenoic acids form the bulk of the unsaturated fatty acid mixture. Thus among the C_{18} polyenoic acid mixture, the tetraenoic acid; among the C_{20} polyenoic acids, the pentaenoic acid; and, finally, among the C_{22} polyenoic acids, the hexaenoic acid are the main constituents of the fractions. In the original acid mixture these most highly unsaturated fatty acids occur in amounts of about 60 to 80 per cent.

Unlike the polyene pigments discussed previously, the double bonds in these acids are not conjugated, the bond positions for tri-, tetra-, penta- and hexa-enoic acids being

3, 6, 9

3, 6, 9, 12

3, 6, 9, 12, 15

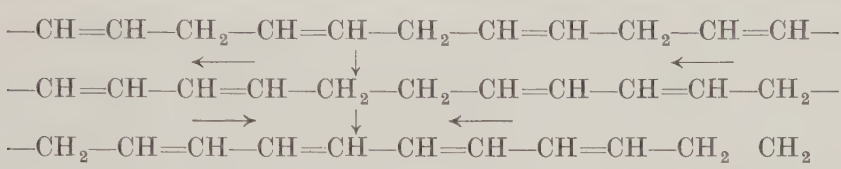
3, 6, 9, 12, 15, 18

These bonds, however, migrate readily into conjugation. There is still some uncertainty as to just how the migration occurs. In the case of a trienoic acid, the conjugation is almost certainly to be 4, 6, 8, i.e.:

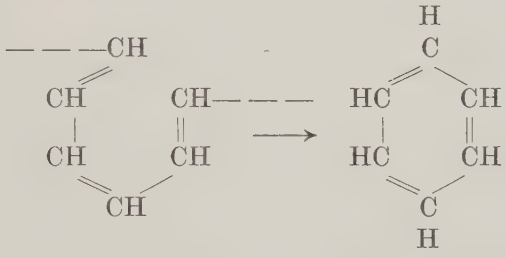
—C—C—C—C=C—C—C=C—

—C—C=C—C=C—C=C—C—

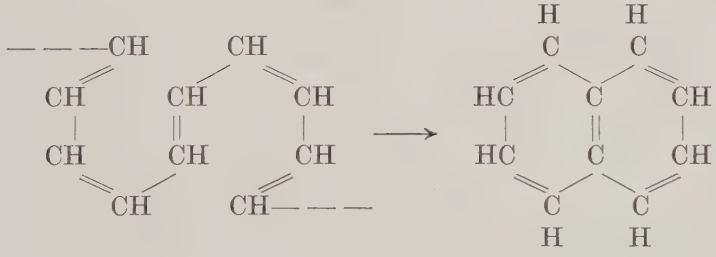
In the case of a tetraenoic acid, KEPPLER (1958) suggests that the reaction may be:



and likewise for the pentaenoic and hexaenoic acids. Whatever the mechanism, HOLMAN (1957) has presented conclusive spectral evidence indicating that migration to full conjugation for six double bonds does take place. With these conjugated unbranched chains, condensation reactions analogous to those for the polyene pigments would be expected to yield the parent aromatics benzene and naphthalene:



benzene



naphthalene

as well as mono- and di-substituted benzenes, naphthalenes and perhaps naphthenes.

Considering the ease with which many of the above reactions go, the build-up of aromatic hydrocarbons in organic-rich sediments should proceed relatively rapidly in terms of geologic time. In fact, the first stages of the genesis may

already have been observed by Emery and Hoggan (1958) who, using an extremely sensitive analytical method, have detected minute quantities of benzene, toluene and the xylenes in certain recent aquatic sediments.

The Low Molecular Weight Aliphatic Hydrocarbons

Another characteristic fraction of crude oils, including the dissolved gas, are the low molecular weight aliphatic hydrocarbons. For convenience, this section will deal primarily with those through C_5. Higher members of the series will be treated in the following section.

The source of these eight hydrocarbons represents a problem somewhat similar to that concerning the source of the low molecular weight aromatic hydrocarbons. Here, it is the lowest member of the series, methane, which is a natural product. Methane is produced in quantity by bacterial fermentation and is the primary hydrocarbon constituent of sediment gases. In such gases, the higher members of the series are present only in negligible quantities (Davis and Squires, 1954).

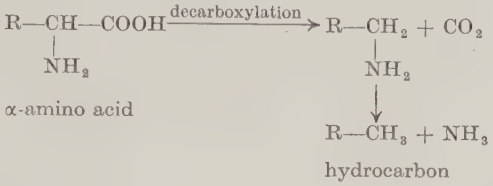
Ethane, propane, the two butanes and the three pentanes are not reported to be constituents of living organisms or as metabolic products. In fact, *n*-heptane is the lowest molecular weight aliphatic hydrocarbon known to be a constituent of a living organism. It is necessary, therefore, again to seek out a chemical mechanism for the genesis of these hydrocarbons.

At present it is believed that protein represents an important source of these low molecular weight aliphatic hydrocarbons. The mechanism proposed involves two steps, decarboxylation and reductive diamination, and is illustrated in Fig. 3. In all, there are about twenty-five common amino acids, of which eleven of the most common are listed in the figure. The proposed reactions will yield all the aliphatic hydrocarbon isomers with the exception of neopentane, which, incidentally, is a relatively rare constituent of petroleum. Although this degradation yields primarily aliphatic hydrocarbons, it should be noted that in one instance at least an aromatic hydrocarbon, ethyl benzene, also would be formed.

Both decarboxylation and deamination reactions can be carried out in the laboratory. Vallentyne (1957) has shown that the first step, the decarboxylation to the amine, can be accounted for by a first-order auto-decomposition under earth conditions, the rate depending upon the stability of the particular amino acid. Relatively less is known about the second step, the reductive deamination. That the reduction must take place is indicated by the fact that the ammonia, a by-product of the reaction, is abundant in petroleum source rocks (Marlett and Erdman, 1959), while amines are absent, or at least have not been detected. Like amines, their loss through solution in interstatial water is unlikely, because of their adsorption on mineral matter, particularly the clays.

To be a source of hydrocarbons, amino acids of protein must be deposited in aquatic sediments in appreciable quantity. Until a few years ago it was believed that these compounds would be destroyed so rapidly by bacteria that they would not survive into the sediments (ZoBell, 1946; Bogomolov, 1954). Doubt was thrown on this view by Abelson (1954, 1955), who showed that traces of the chemically more stable amino acids remained in fossil bones and shells. Studies in

General reaction—



Amino acid	*Hydrocarbon Residue*
alanine $CH_3—CH(NH_2)—COOH$	ethane $CH_3—CH_3$
α-amino-*n*-butyric acid $CH_3—CH_2—CH(NH_2)—COOH$	propane $CH_3—CH_2—CH_3$
arginine $H_2N—C(=NH)—NH—CH_2—CH_2—CH_2—CH(NH_2)—COOH$	*n*-butane $CH_3—CH_2—CH_2—CH_3$
aspartic acid $HOOC—CH_2—CH(NH_2)—COOH$	ethane $CH_3—CH_3$
glutamic acid $HOOC—CH_2—CH_2—CH(NH_2)—COOH$	propane $CH_3—CH_2—CH_3$
glycine $CH_2(NH_2)—COOH$	methane CH_4
*iso*leucine $CH_3—CH_2—CH(CH_3)—CH(NH_2)—COOH$	*iso*pentane $CH_3—CH_2—CH(CH_3)—CH_3$
leucine $CH_3—CH(CH_3)—CH_2—CH(NH_2)—COOH$	*iso*pentane $CH_3—CH(CH_3)—CH_2—CH_2$
lysine $CH_2(NH_2)—CH_2—CH_2—CH_2—CH(NH_2)—COOH$	*n*-pentane $CH_3—CH_2—CH_2—CH_2—CH_3$
phenylalanine $C_6H_5—CH_2—CH(NH_2)—COOH$	ethylbenzene $C_6H_5—CH_2—CH_3$
valine $CH_3—CH(CH_3)—CH(NH_2)—COOH$	isobutane $CH_3—CH(CH_3)—CH_3$

Fig. 3. The amino acids as a possible source of low molecular weight hydrocarbons.

	Upper Anahuac Shale	Lower Anahuac Shale		Vicksburg Shale	La Luna Limestone
	DXXIII-C	DCXXIII-B	DCXXIII-C	DCCXXIII-A	DXXIX-A
Alanine	+++*	+++	+++	+++	+++
Aspartic acid	−	<+	−	−	−
Glutamic acid	+	++	+	<+	+
Glycine	+	+	+	+	++
Leucines	++	+	++	++	++
Proline	+	+	+	+	+
Valine	++	+	++	+	+
Unknown A†	+	+	+	+	+

* The "+" signs indicate the order of abundance: +++ high, ++ medium, + low. The "−" signs indicate that the compound was sought but not detected within the sensitivity limits of the method.

† Resembles but is not identical to serine.

Fig. 4. Amino acids identified in ancient sediments and their relative order of abundance.

this laboratory (Marlett and Erdman, 1959) further showed that similar traces existed in fine-grained Oligocene and Cretaceous shales and limestone. The array of amino acids found in these samples is shown in Fig. 4. The amounts, shown in Table 12, however, are negligibly small as contrasted to the total reduced nitrogen, the major portion of which is ammonia.

In contrast with the ancient rocks, recent sediments were found to contain most of the common amino acids. Those which have been identified and their relative abundance are shown in Fig. 5. Some variation in relation to environment

Amino acid	Near-shore marine CCCX-B				Mississippi Sound CCCXVIII-A				Northern Fresh-water swamp CCCXXVII-B
	Loc. 1	Loc. 2	Loc. 3A	Loc. 4	Loc. 1	Loc. 2	Loc. 3	Loc. 4	Loc. 1
Alanine	+++†	+++	++	+++	+++	+++	+++	+++	+++
α-Amino-*n*-butyric acid‡	−	−	−	−	−	−	−	−	+
Arginine	−	−	−	−	−	−	−	<+	<+
Aspartic acid	++	+	++	++	++	++	++	++	++
Glutamic acid	+	++	++	++	++	++	++	++	+++
Glutamine‡	−	<+	−	<+	+	−	+	+	+
Glycine	++	+++	++	+++	+++	+++	+++	+++	++
Histidine		<+		<+		<+		+	+
Hydroxyproline	−	−	−	−	−	−	−	−	++
Leucines	+++	+++	+++	+++	++	++	++	++	+++
Lysine		+		<+		+		+	++
Methionine	−	−	−	−	−	−	−	−	−
Methionine sulfoxide‡	−	−	−	−	−	−	−	−	+
Phenylalanine	+	+	+	+	++	+	++	+	+
Proline	++	++	++	++	++	++	++	++	++
Serine	−	<+	−	+	<+	+	<+	+	++
Threonine	−	+	−	+	−	+	−	+	++
Tryptophan	−	−	−	−	−	−	−	−	−
Tyrosine	++	+	++	+	++	+	++	+	++
Valine	+++	+++	+++	+++	+++	++	+++	++	++
Unknown A§	−	−	−	+	−	+	−	+	+
Unknown B*	−	<+	−	+	−	−	−	+	−

† The "+" signs indicate the order of abundance: +++ high, ++ medium, + low. The "−" signs indicate that the compound was sought but not detected within the sensitivity limits of the method.

‡ Identification tentative.

§ Unknown A is detected by the platinic iodide test for cystine, cysteine, methionine and other reducing substances.

* Unknown B occupies a spot not taken by the common amino acids. It may be hydroxyglutamic acid.

Fig. 5. Amino acids identified in recent sediments and their relative order of abundance.

may be noted. The amounts of amino acids, unlike those in the ancient rocks, however, are not small. As is shown in Table 13 the amino acids represent an appreciable amount of both the organic carbon and total reduced nitrogen in these samples. Calculation indicates that their concentration is more than sufficient to provide the requisite amount of C_1 through C_5 aliphatic hydrocarbons, even assuming the limiting condition that all the organic carbon in the semi-marine and sound samples was converted to petroleum. The apparent failure for this reaction to proceed under swamp conditions is at present unknown.

Intermediate and High Molecular Weight Hydrocarbons

The origins of the intermediate and high molecular weight aromatic hydrocarbons in source sediments of petroleum and the crude oils which they have produced are probably diverse. Only a few of the many possibilities will be discussed here.

Beginning with *n*-neptane and *p*-cymene, many of these compounds are normal constituents of the lipid fraction of plants and animals. Because of their chemical stability, such compounds might be expected to survive throughout geologic time with relatively little structural change.

Almost certainly, many of these compounds also are generated from non-hydrocarbon source material. Probable precursors are the saturated and unsaturated fatty acids, aldehydes and alcohols, including the polycyclic sterols. That the necessary reactions required to bring about the elimination of the functional groups can go under earth conditions, is fairly conclusive. It is known that as the carbon chain of an aliphatic acid increases in length, decarboxylation proceeds more readily. In petroleum and the waters associated with it, acetic acid is fairly abundant. The amounts of propionic acid, butyric acid and, finally, valeric acid decrease progressively toward the vanishing point. The indication is that decarboxylation of the longer acid chains has proceeded essentially to completion. Additional evidence is provided by the fact that aliphatic acid side chains of the chlorophyll and haeme or haematin derivatives in crude oil, for the most part, have been decarboxylated (Treibs, 1936). Similar evidence exists for elimination of hydroxy and carbonyl groups.

Asphaltic Constituents

Asphaltic constituents are defined here as the dark-coloured, non-hydrocarbon fraction of petroleum and of the organic portion of source rocks. In addition to carbon and hydrogen, these constituents contain primarily oxygen, nitrogen and sulphur. The molecular weights of those in petroleum range probably from a few hundred to a hundred thousand or more; quantitatively, they represent from a trace in some crudes to more than 60 per cent in others. On the other hand, the molecular weight range of these constituents in source rocks seems to extend to much higher values, with concomitant decrease in solubility in organic solvents.

A variety of data indicate that, at least for a given crude and source rock, the larger portion of the asphaltic fraction comprises a family of chemically closely related compounds. Molecular weight studies using the ultracentrifuge indicate a continuous gradation of molecular weights. Fractionation according to molecular

weight using the ultracentrifuge, or by solubility, yields series of fractions with much the same elemental analysis and infra-red spectral absorption. In the visible and ultra-violet, the spectral absorption curves are devoid of structure, being characterized by progressively higher values of the extinction coefficient with decreasing wavelength. Plotted as a function of increasing molecular weight, or decreasing solubility, a family of curves is obtained, the values of the extinction coefficient rising more rapidly at longer wavelengths. X-ray diffraction studies indicate aromatic fused ring sheets intermixed with aliphatic chains.

Efforts have been made in this laboratory to compare the chemical properties of asphaltic fractions from crude oils and from source rocks, with each other and with other ancient carbonaceous material, such as coals and oil shales. Rate of oxidation has proved a useful tool for the purpose. Comparing the oxidation rates of the higher molecular weight solid fraction of petroleum asphaltics, small but significant differences have been observed. In contrast, the oxidation rates of coals and oil shale are much higher, denoting a considerable difference in structure.

Discussion of the source of the asphaltic constituents in petroleum and source rocks is handicapped by the limited knowledge of their structure. These substances definitely are not produced by plants and animals, and no true asphaltic material has been observed in an uncontaminated recent sediment.

Probably a number of classes of plant and animal products have contributed to the structure of the asphaltics. The evidence for fused ring centres strongly suggests that cellulose may have been a contributor, the more aliphatic matrix being provided by lignin. Nitrogen heterocycles may have been derived from such compounds as purines and pyrimidines. Sulphur in the structure probably has been derived largely through reaction with the element late in the process of genesis.

Conclusion

At the beginning of this paper, source sediments of petroleum were defined as those rocks in which appreciable quantities of crude oil have been generated. The criterion for genesis of crude oil was the formation in appreciable quantities of all the major constituents, namely, the low molecular weight aromatic and aliphatic hydrocarbons, the higher molecular weight hydrocarbons and the asphaltics.

Throughout the discussion, it has been indicated that in certain rocks a higher proportion of the organic matter initially deposited in the sediments is converted into constituents of petroleum. The major fractions of petroleum almost certainly are formed from particular classes of plant and animal compounds. Composition, or at least the relative abundance of these chemical precursors, varies throughout the plant and animal kingdoms. Thus, the environment, as it affects the ecology, would affect the composition of the source material. Whether other environmental factors enter by altering the course of the degradations of the chemical source material is at present unknown. Certainly, the trend shown in Table 13 would indicate that post-depositional factors might affect the course of degradation of the amino acids.

Finally, it is believed that the proportion of the organic material converted to petroleum in the rock is more significant than the absolute amount formed. In the freshly deposited sediments, the highly polar constituents of the organic

fraction are preserved from loss during the early expulsion of water by adsorption on mineral constituents of the sediment. As functional groups are lost to form the weakly polar constituents of petroleum, the association with the mineral matter weakens. At the same time, however, attraction to the relatively hydrophobic surfaces of solid carbonaceous matter increases. The retentivity of the sediment during compaction for the constituents of petroleum thus becomes a function of the amount of solid carbonaceous material. Dynamically, the carbonaceous material will retard migration of the constituents of petroleum. If the amount of the latter is sufficiently high in proportion to the insoluble solid carbonaceous material, the process will tend merely to concentrate the constituents of petroleum until they break out of the fine-grained sediment. If the proportion of the migrating organic material is too small in proportion to the stationary carbonaceous material, migration will be too slow to permit the former to escape from the sediment. Thus, it is not unreasonable that rocks like the Anahuac shale of Texas with a relatively low total carbon content probably have been responsible for crude oil deposits in quantity while the Green River oil shale and most coals, with a higher content of gaseous and liquid hydrocarbons and other petroleum constituents, apparently have failed to yield oil.

In conclusion, it is believed that the recognition of source sediments of petroleum will not likely be accomplished through application of any single test. Rather, recognition of a rock as having been a prolific source of oil, or of varying smaller amounts, of none at all, will remain a matter of judgement. The ability to achieve diagnostic precision, however, should grow with an increasing understanding of the chemical reactions which plant and animal detritus undergo when buried in the earth.

Acknowledgements—This work was sponsored by the Gulf Research & Development Company as a part of the research programme of the Multiple Fellowship on Petroleum.

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Distribution of hydrocarbons in sedimentary rocks

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Abstract—Free liquid and solid hydrocarbons comparable to those in petroleum are constituents of practically all sedimentary rocks. The quantities vary from a few parts per million in continental deposits to several thousand parts per million in bituminous marine shales. Associated with this oil are two other substances—a soluble asphalt, and an insoluble pyrobituminous material called kerogen.

There is no systematic change in the hydrocarbon content of sedimentary rocks with depth or age. The biggest variations seem to be between different formations and different facies of the same formation. Metamorphism appears to decrease the hydrocarbons and to alter the kerogen of a rock.

Comparisons of reservoir hydrocarbons with the hydrocarbons from their presumed source rocks show that the latter tend to contain a greater percentage of aromatic hydrocarbons.

Commercial accumulations of hydrocarbons in reservoir rock represent only a fraction of the total hydrocarbons estimated to exist in a finely disseminated form in practically all sedimentary rocks of marine origin.

Introduction

Most geologists now agree that petroleum is generated in sedimentary basins from the organic residue of plants and animals that were deposited with the sediments. In recent years a better understanding of this process has resulted from detailed studies of the organic matter in sediments. The most significant result of these studies was the discovery of free liquid and solid hydrocarbons in the non-reservoir sections of a depositional basin, that is, the shales and limestones that are presumed to be the source beds of petroleum. Studies by Smith (1954), Meinschein (1957), and Stevens (1958) on recent sediments, and Phillipi (1956), and Hunt and Jamieson (1956) and Hunt and Meinert (1958) on ancient sediments have revealed that hydrocarbons, comparable to those found in crude oil, are a constituent of practically all sediments.

Although the occurrence of hydrocarbons in sediments is universal, the quantities vary from a few parts per million to several thousand parts per million. The reasons for these variations are unknown, but they would be expected to show some relationship to geologic parameters such as the environment of deposition, rate of compaction, geologic age, etc. For example, the stagnant highly reducing environment in the deeper portions of some silled basins would be expected to preserve more hydrocarbons than the oxidizing environment in which redbeds are deposited. The rapid deposition of clay muds during periods of wide-spread tectonic activity might form and preserve hydrocarbons differently than would the quiet deposition of carbonate muds.

The present studies were undertaken in an effort to learn more about the relation of hydrocarbon distribution to geologic parameters and thereby to better understand the reasons for hydrocarbon variations. The first part of this paper very briefly reviews the method of extracting hydrocarbons from rocks, and compares hydrocarbon composition with that of crude oil. The major part of the paper deals with variations in hydrocarbon distribution with geologic factors.

Composition of Hydrocarbons in Sediments

Method of separation

The technique used in this study for separating hydrocarbons from sediments has been described in detail in previous publications (Hunt and Jamieson, 1956; Hunt and Meinert, 1958). Basically, the method consists of grinding the rock to a very fine powder and extracting it with a mixture of 70% benzene, 15% acetone, and 15% methanol. The extract consists of hydrocarbons and nonhydrocarbons (asphalt), which are separated by chromatography. The extracted rock is analysed for organic carbon, and the organic matter (kerogen) remaining in the rock is estimated by multiplying the organic carbon content by 1·22. This factor was determined by Forsman and Hunt (1958) from the analysis of 21 organic residues obtained by dissolving the mineral matter of extracted shales and limestones with hydrofluoric and hydrochloric acids.

Comparison of hydrocarbons from nonreservoir rock with crude oil

A previous study by the writer (Hunt and Jamieson, 1956) showed that the hydrocarbons extracted from ancient non-reservoir rocks are similar in their general properties to the heavier hydrocarbons found in associated reservoirs. They have a boiling range comparable to the 400° F plus fraction of crude oils, and are composed primarily of the same paraffin, naphthene and aromatic structures found in crudes.

This previous work also compared the distribution of hydrocarbon types in a crude oil from the Wall Creek sand in Wyoming and the hydrocarbons extracted from its presumed source rock, the Frontier shale. A close similarity was found between the source and reservoir oil. However, subsequent studies suggest this was fortuitous and that source hydrocarbons frequently contain a higher percentage of aromatic structures than the corresponding reservoir hydrocarbons. For example, Fig. 1 shows the locations of two oil-source rock pairs that are about as closely related as a geologist can obtain. The Cherokee shale completely surrounds the Bartlesville sand, and samples of oil were extracted from the shale both above and below this sand. Subsequent analyses of these two shale oils showed them to be practically identical in composition. Oil was also extracted from a Woodford shale sample taken a few feet above Misener sand oil production.

In Fig. 2 the compositions of the crude oils in the Bartlesville and Misener sands are compared with the compositions of the oils extracted from their presumed source rocks, the Cherokee and Woodford shales. In both examples the source rock oil has more aromatic and fewer paraffin and naphthene hydrocarbons than the reservoir oil.

Recent studies by Brenneman and Smith (1958) also indicate that hydrocarbons extracted from source rocks differ in hydrocarbon-type distribution from those in the associated reservoirs. A comparison of their results on eight pairs of source and reservoir oils shows that most of the source oils contained more aromatic hydrocarbons than the reservoir oils.

Although the data obtained to date are limited, it does appear that there is some mechanism that tends to concentrate aromatic hydrocarbons in the source

sediments. This could be either a fractionation of oil in the process of migrating from source to reservoir, or the generation of more aromatics in the source rock with time.

Distribution of Hydrocarbons in Sediments

Recent and ancient sediments

Recent sediments can be analysed for their hydrocarbons and related organic matter by the same procedures used for ancient sediments. Average hydrocarbon values and ranges for samples from several recent sediment areas are shown in

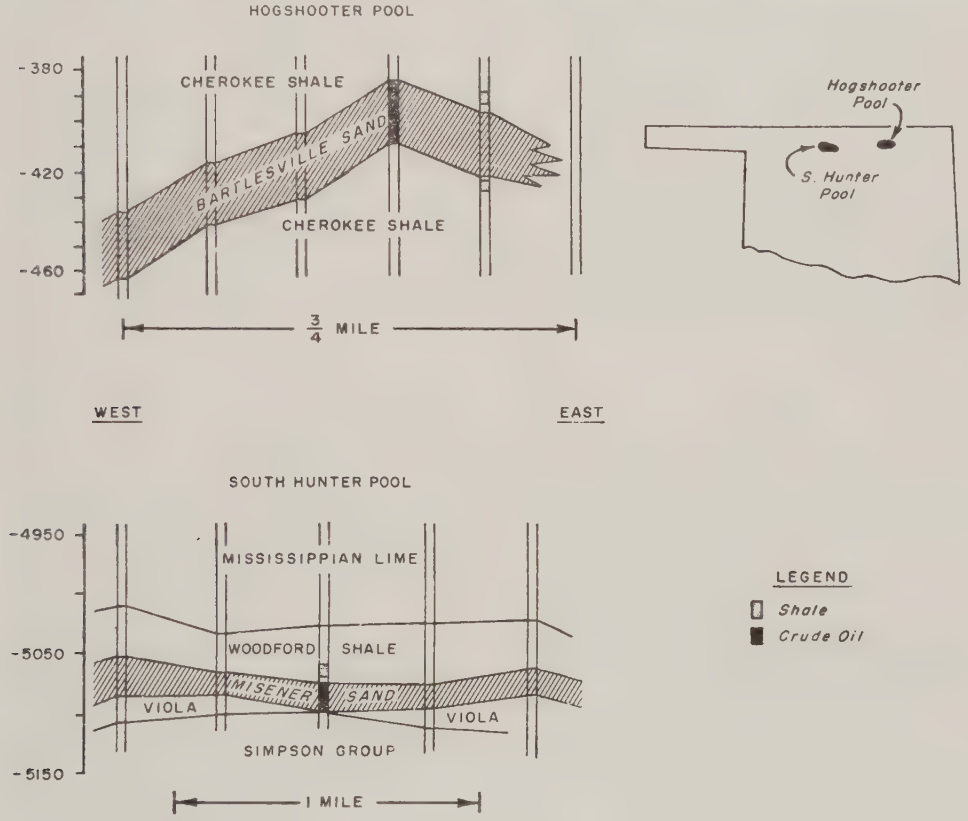
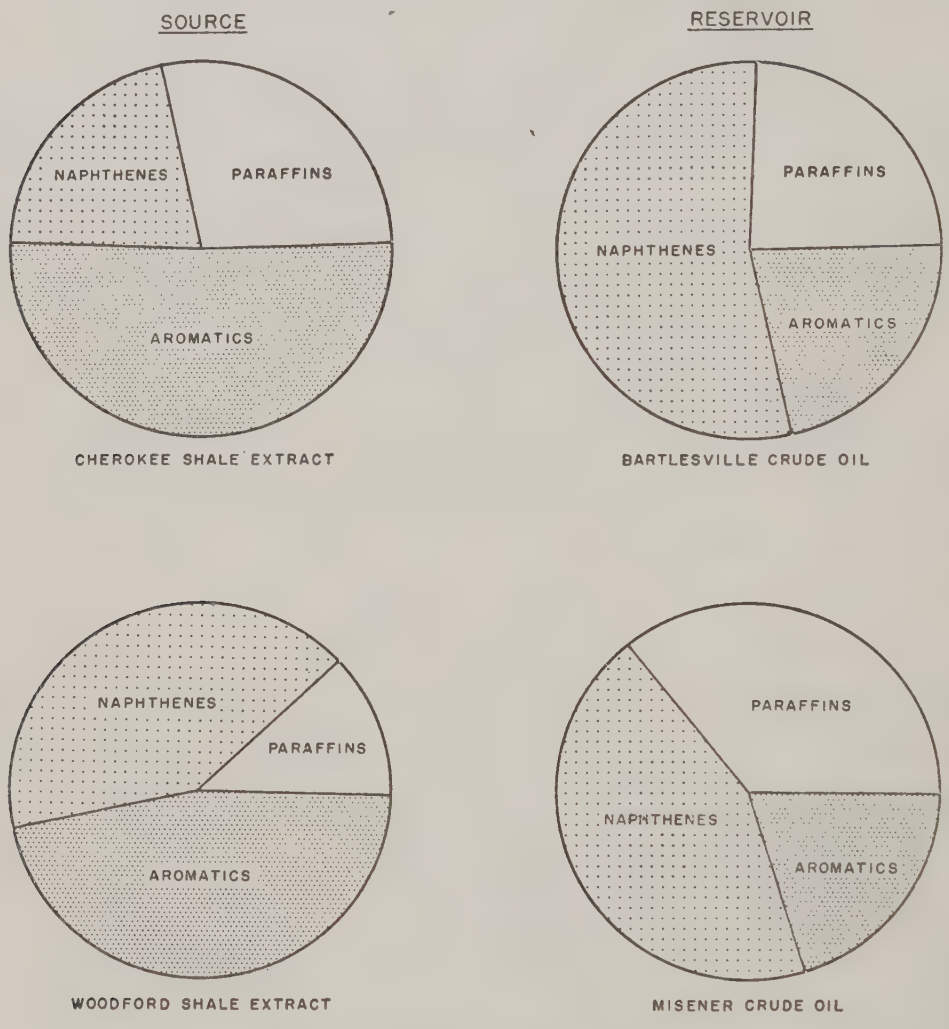


Fig. 1.

Table 1 along with data for their associated organic matter—asphalt and kerogen. Average values for a large number of ancient shales and carbonates are shown for comparison. These ancient rocks are sub-surface samples from about 200 formations in sixty-sedimentary basins. One-third of the rocks are from the United States, the rest being from Canada, Venezuela, Colombia, Peru, Guatemala, Australia, New Guinea, India, Pakistan, British Somaliland and Denmark.

Although the number of recent environments examined is admittedly limited

compared with the many environments of deposition represented by the ancient rocks, it is interesting to note that the average hydrocarbon content of all of the recent mud samples is considerably lower than the average value for the ancient



COMPARISON OF OIL EXTRACTED FROM RESERVOIR SAND AND OIL IN THE PRESUMED SOURCE ROCK

Fig. 2.

samples. There are three possible explanations for this: (1) some hydrocarbons may form with time, (2) none of the recent areas may be comparable in organic deposition to the environments under which the average ancient sediments were deposited, and (3) the recent environments may be less favourable for organic preservation than those of the average ancient sediments.

Variations in hydrocarbon distribution with lithology

Lithologic changes generally are accompanied by changes in the concentration of hydrocarbons, as shown in Table 2 (the associated asphalt and kerogen is shown for comparison). These are typical examples chosen from a group of about 1000 analyses. The calcareous and dolomitic marine shales are generally high in hydrocarbons. In contrast, green shales, red shales and Pre-Cambrian sedimentary rocks

Table 1. Distribution of hydrocarbons and associated organic matter in recent and ancient non-reservoir sediments

	No. samples	Average composition and ranges (p.p.m.)*		
		Hydrocarbon	Asphalt	Kerogen
Recent sediments†				
Mediterranean Sea	1	29	461	9000
Gulf of Mexico	10	32 (12–63)	275 (113–790)	6400 (3800–9100)
Gulf of Batabano, Cuba	10	40 (15–85)	575 (136–1023)	17,100 (2900–34,900)
Orinoco Delta, Venezuela	10	60 (27–110)	555 (283–1355)	10,500 (7500–14,700)
Lake Maracaibo, Venezuela	8	68 (24–116)	1060 (266–1600)	26,900 (13,700–41,500)
Cariaco Trench, Venezuela	16	105 (56–352)	1250 (224–2600)	25,000 (8100–31,200)
Ancient sediments				
Shales	791	300	600	20,100
Carbonates	281	340	400	2160

* Ranges for recent sediments are shown in parentheses. Ranges for ancient sediments are in Table 5. In this and subsequent tables the hydrocarbon is defined as the organic matter extracted from the rock that contains only the elements, carbon and hydrogen. The asphalt is the soluble non-hydrocarbon material and the kerogen is the insoluble organic matter remaining in the rock. All yields in this text are reported on a dry sample-weight basis.

† All samples are clay muds except those from the Gulf of Batabano, which are carbonate.

contain very small amounts of hydrocarbons. The green shales probably represent environments that deposited very little organic matter. Oxidation has probably destroyed the hydrocarbons and organic matter of the red rocks, whereas the low values for the Pre-Cambrian samples are probably due to metamorphism. Metamorphism definitely lowers the hydrocarbon and organic content of a rock. This is evident from the analyses of the metamorphosed and unaltered samples of Pierre shale from Colorado.

Major lithologic changes within the same time depositional unit may be accompanied by marked changes in the quantity of hydrocarbons and organic matter. During the Permian age, the Phosphoria sea came down into Wyoming from the north-west and deposited thick sections of grey argillaceous carbonate intermingled with black calcareous shales. To the east, the time equivalent of this Phosphoria is a redbed-evaporite sequence. The facies change from grey carbonates to redbeds is accompanied by a sizable decrease in both hydrocarbons and organic matter, as noted in Table 3. Here it is apparent that little organic matter was deposited or preserved in the redbeds because of the oxidizing environment.

Table 2. Distribution of hydrocarbons and associated organic matter in non-reservoir rocks of various lithologies

	Composition (p.p.m.)		
	Hydrocarbon	Asphalt	Kerogen
Shales			
Steele (7-34N-75W, Wyoming)	120	430	7650
Wilcox (48-6N-9E, Louisiana)	180	660	9660
Cherokee (6-36S-5E, Kansas)	230	670	22,100
Bell (20-19N-17W, Michigan)	300	190	4510
Frontier (28-46N-82W, Wyoming)	300	940	14,560
Springer (23-2N-3W, Oklahoma)	400	600	17,000
Monterey (12-25S-12E, California)	500	2300	22,000
Caney (8-1N-1W, Oklahoma)	900	2700	43,400
Woodford (36-26N-5W, Oklahoma)	3000	3500	53,500
Calcareous Shales			
Niobrara (27-36N-79W, Wyoming)	1100	1900	36,200
Traverse (20-19N-17W, Michigan)	1120	2050	12,230
Antrim (20-19N-17W, Michigan)	2400	4490	67,110
Duvernay (LSD 16-6-48-24W4, Alberta)	3300	6500	78,700
Nordegg (LSD 12-13-77-21W5, Alberta)	3800	10,800	126,100
Limestones and Dolomites			
Mission Canyon Ls (12-36N-47E, Montana)	67	98	1135
Ireton Ls (24-59N-26W4, Alberta)	106	250	2845
Madison Dol (29-14N-60E, Montana)	243	365	1325
Charles Ls (29-14N-60E, Montana)	271	665	3165
Zechstein Dol (Denmark)	310	590	2486
Banff Ls (7-163N-102W, North Dakota)	530	308	4653
Madison Ls (27-29N-51E, Montana)	2133	360	5620
Red Shales			
Chugwater (25-3N-82W, Colorado)	13	32	455
Big Snowy (27-28N-51E, Montana)	14	26	460
Big Snowy (27-28N-51E, Montana)	17	60	4220
Green Shales			
Pliocene (Lake Maracaibo, Venezuela)	10	80	410
Big Snowy (27-28N-51E, Montana)	15	20	965
Tertiary (Middle Magdalena Valley, Colombia)	20	160	6520
Ireton (LSD 15-14-48-23-W4, Alberta)	23	47	1270
Pre-Cambrian Rocks			
Thomson slate (Outcrop, Minnesota)	16	58	1626
Virginia argillite (Outcrop, Minnesota)	30	44	1926
Cuyana argillite (Outcrop, Minnesota)	79	41	1180
Metamorphosed Pierre Shale (10-3N-81W, Colorado)	29	111	8760
Unmetamorphosed Pierre Shale (10-3N-81W, Colorado)	130	470	13,600

Variations in hydrocarbon distribution with rock depth

Because of the wide variation in hydrocarbon distribution with lithology, other comparisons with geologic parameters were made with rocks of uniform lithology.

Hydrocarbon variations with depth in two shales of uniform lithologic character are shown in Table 4. The 10-ft section of Lakota shale is a dark grey silty shale with uniform density texture and mineralogical composition. In this very short

section, the hydrocarbon content varies by a factor of more than 2 for no apparent reason other than possible differences in the environment of deposition which are not reflected in lithology.

The 1700-ft section of Hoxbar shale is a dark grey shale also having a uniform textural and mineralogical composition. There is a sizeable difference in hydrocarbon and associated organic matter content of the sample at 10,400 ft compared

Table 3. Distribution of hydrocarbons and associated organic matter in Phosphoria formation of Wyoming

Location	Sample description	Composition (p.p.m.)		
		Hydrocarbon	Asphalt	Kerogen
58N-100W, Wyo.	Grey argillaceous dolomite	300	750	2850
33N-92W, Wyo.	Grey argillaceous dolomite	500	350	1135
37N-79W, Wyo.	Red silty shale	15	15	470

Table 4. Change in hydrocarbons and associated organic matter with depth in a uniform lithology

Sample and depth (ft)	Composition (p.p.m.)		
	Hydrocarbon	Asphalt	Kerogen
Lakota shale (10-ft section)			
3829	147	313	15,140
3832	170	570	11,260
3837	68	332	13,000
3839	90	660	6550
Hoxbar shale (1700-ft section)			
10,400	600	700	28,700
10,700	100	140	9760
11,080	200	300	6800
12,100	140	100	5660

with that of the others. Here again, it appears that the environment of deposition varies sufficiently to preserve greater quantities of hydrocarbon and other organic matter at different times without appreciably altering other characteristics of the shale.

Variations in hydrocarbon distribution with rock density

As the sediments of a basin are compacted, the water is squeezed out and the oil presumably is carried with it. If other factors are assumed to be constant, the denser rocks containing less water would be expected to contain less oil also. In Fig. 3 the per cent hydrocarbon in the total organic matter is plotted against density for 360 shales. Per cent hydrocarbon instead of total hydrocarbon is plotted partially to compensate for the effect of variations in total organic matter. The flat lines represent average hydrocarbon values for all samples within the

density range of the lines. Contrary to expectations, there appears to be an increase in the hydrocarbons with increasing density. This change is not gradual or systematic, but somewhat abrupt, with the biggest change at densities beyond 2·4. This change suggests that hydrocarbons may be forming in the denser and deeper rocks, or it could mean that there was better preservation of hydrocarbons at the time the denser rocks were deposited. The latter interpretation seems improbable in view of the variety of depositional environments from which this large number of samples was taken.

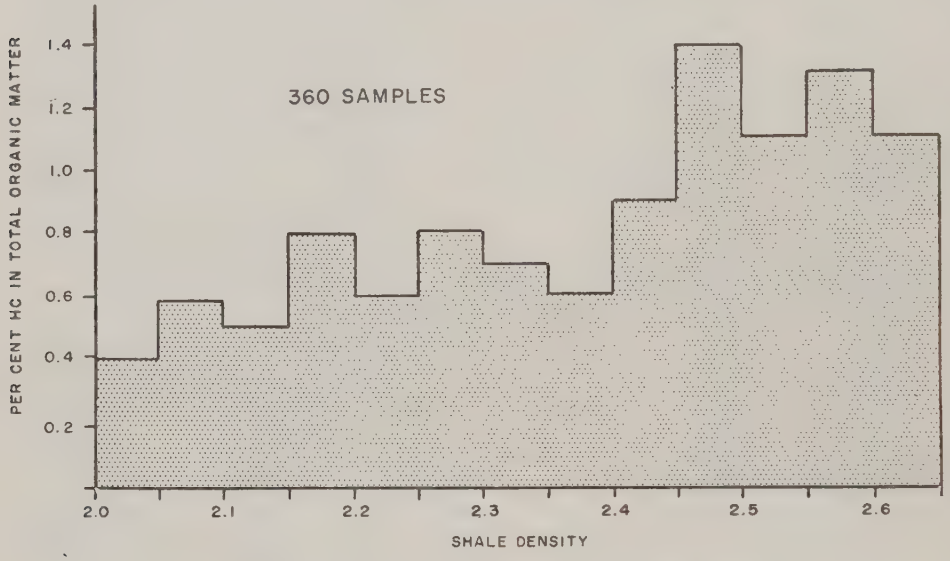


Fig. 3. Variation in hydrocarbons with shale density

Distribution of Hydrocarbons and Total Organic Matter in Non-reservoir Shales and Carbonates

In this study we were interested in determining hydrocarbon and organic distributions in the two more common non-reservoir lithologies—shales and carbonates. The distribution curves for hydrocarbons in these lithologies are shown in Fig. 4. Here the hydrocarbon content in parts per million is plotted on a logarithmic scale on the abscissa and the per cent of total samples on an arithmetic scale on the ordinate. Essentially pure shales and carbonates were used in this comparison, the highly argillaceous carbonates and calcareous shales being eliminated. It is evident from a comparison of the logarithmic means that about half the samples contain more than 100 p.p.m. hydrocarbons and about half contain less.

When the data are recalculated to obtain an arithmetic average, it is found that the shales average 300 p.p.m. hydrocarbon and the carbonates average 340 p.p.m. hydrocarbon.

A similar comparison for the total organic matter can be made, as shown in Fig. 5. Here the total organic matter in weight per cent is plotted on a logarithmic scale on the abscissa and the per cent of total samples on an arithmetic scale on the ordinate. In this case there is a very significant difference in organic matter

distribution. About half of the shales contain more than 1 per cent organic matter, whereas nearly all of the carbonates are below this value. The carbonates are also unusual in that there is a sudden increase in the front part of the curve, compared with a gradual increase for the shales. The data from which these curves were constructed is given in Table 5. Since hydrocarbon analyses were not made on all samples, the carbonate curve for total organic matter is based on a larger number of samples than the carbonate curve for hydrocarbons.

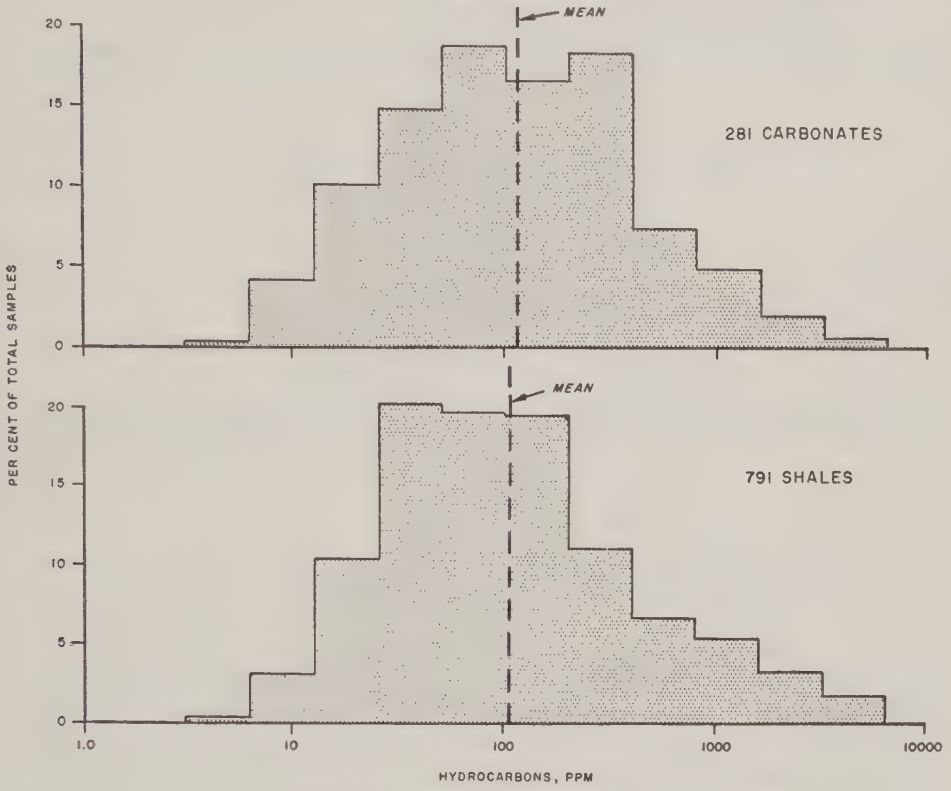


Fig. 4. Hydrocarbon content of sedimentary rocks in p.p.m.

Recalculating the data to obtain an arithmetic average gives 2·1 weight per cent organic matter in shales and 0·29 weight per cent organic matter in carbonates. The low organic content of the carbonates results in a much higher ratio of hydrocarbons to total organic matter in carbonates than in shales.

Comparison of the volume of hydrocarbons accumulated in reservoirs with that remaining in non-reservoir rock

In a previous publication (Hunt and Jamieson, 1956) the writer estimated the total hydrocarbons in the reservoir and non-reservoir rock of a single formational unit within a limited area of a sedimentary basin. The purpose of that study was to determine if the quantity of hydrocarbons remaining in the source rock was less than or greater than the amount that accumulated in associated reservoirs.

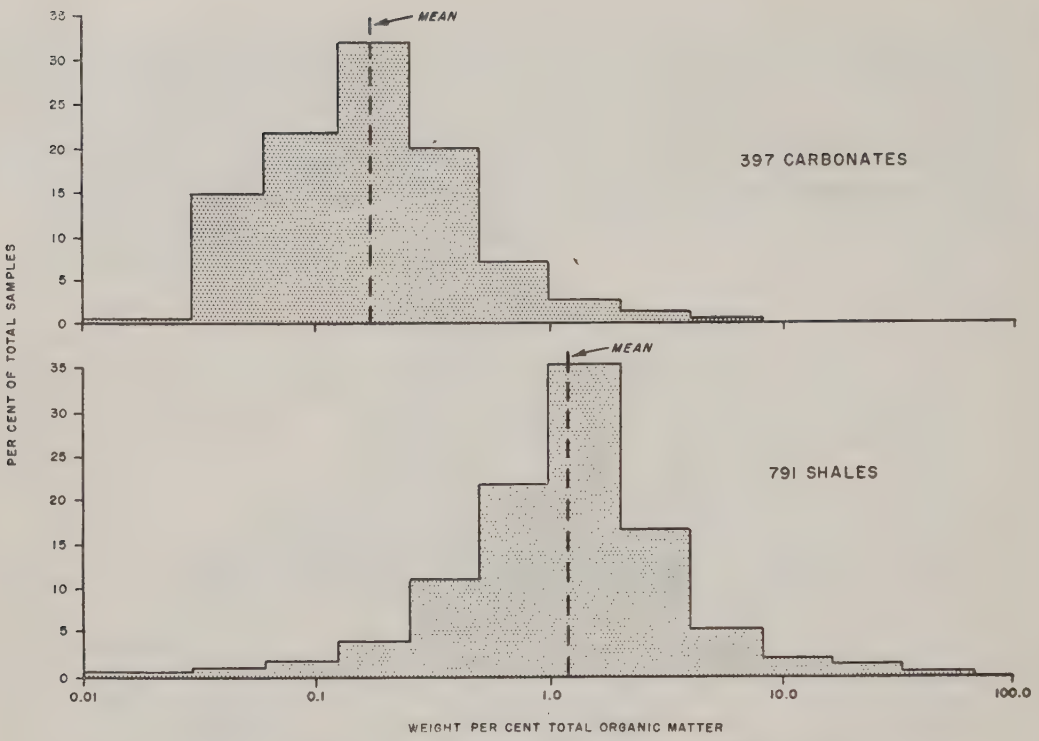


Fig. 5. Weight per cent total organic matter in sedimentary rock

Table 5. Distribution of hydrocarbons and total organic matter in shales and carbonates

Hydrocarbons			Total organic matter		
Range of HC (p.p.m.)	Distribution as % of total		Range of OM as % of rock	Distribution as % of total	
	Shales	Carbonates		Shales	Carbonates
0–3·1	0·0	0·0	0·00–0·031	0·1	0·5
3·1–6·2	0·3	0·4	0·031–0·062	0·7	14·9
6·2–12·5	3·0	4·3	0·062–0·125	1·5	21·9
12·5–25	10·3	10·3	0·125–0·25	3·9	32·0
25–50	20·0	14·9	0·25–0·50	11·1	19·9
50–100	19·4	18·9	0·50–1·0	22·0	7·1
100–200	19·3	16·7	1·0–2·0	35·3	2·3
200–400	11·8	18·5	2·0–4·0	16·6	1·3
400–800	6·4	7·5	4·0–8·0	5·2	0·3
800–1600	5·2	5·0	8·0–16·0	1·8	0·0
1600–3200	2·5	2·1	16·0–32·0	1·6	0·0
3200–6400	1·5	0·7	32·0–64·0	0·1	0·0
6400–12800	0·0	0·7			
No. of samples	791	281		791	397
Logarithmic mean	103 p.p.m.	112 p.p.m.		1·2%	0·17%
Arithmetic mean	300 p.p.m.	340 p.p.m.		2·1%	0·29%

The area chosen for study covered 800 miles^2 along the south-west side of the Powder River Basin in Wyoming. The formation studied was the Frontier, a Cretaceous unit about 1100 ft thick. The unit contained 900 ft of shale and about 200 ft of sand in the form of lenses distributed throughout the formation. The oil in the sands is believed to have originated in the surrounding shale.

The calculation showed that the non-reservoir Frontier shale in this area still contained 3×10^9 barrels of oil. The lenticular reservoir sands contained $0{\cdot}5 \times 10^9$ barrels of oil recoverable by primary methods. Since the total oil in place is roughly three times primary oil, the total reservoir oil was estimated to be $1{\cdot}5 \times 10^9$ barrels or about half the non-reservoir oil.

Table 6. Estimated volume of hydrocarbons in reservoir and non-reservoir rock of the Cretaceous formations of the Powder River Basin in Wyoming
(Total area approximately 15,000 miles^2)

Formation	Average shale thickness (ft)	Estimated oil in shale (barrels)	Estimated oil in reservoir sands (barrels)
Pierre-Steele	3100	74×10^9	520×10^6
Niobrara	450	85×10^9	2×10^6
Frontier-Carlile	750	27×10^9	3000×10^6
Mowry	250	$4{\cdot}25 \times 10^9$	0
Thermopolis-Skull Creek	150	$4{\cdot}25 \times 10^9$	400×10^6
Dakota-Fuson-Lakota	50	$1{\cdot}5 \times 10^9$	2680×10^6
Total	4750	196×10^9	6602×10^6

$$\text{Ratio of } \frac{\text{oil in shale}}{\text{oil in reservoir}} = \frac{196 \times 10^9}{6{\cdot}6 \times 10^9} = \frac{30}{1}$$

Subsequently these calculations were extended horizontally to cover the entire portion of the Powder River Basin in Wyoming, an area of approximately 15,000 miles^2. The non-reservoir shale in this entire area contains about 27×10^9 barrels of oil, whereas the total oil known to exist and expected to be found in this formation is unlikely to exceed 3×10^9 barrels. This means that the volume of hydrocarbons remaining in the Frontier source shale is nine times greater than the volume accumulated in Frontier reservoirs in Wyoming.

Extending these calculations vertically through the entire Cretaceous section of this area makes the quantity of oil in the sand appear to be an even smaller fraction of the total oil. Table 6 contains estimates of the volume of oil in all Cretaceous sediments in the Wyoming part of this basin. Volumes in the shales were estimated from analyses of shale samples in this area. Volumes in the reservoir sands were estimated from production data and the "best guesses" of geologists familiar with the area as to the quantity of oil that will ultimately be found. The data indicate that the non-reservoir Cretaceous rocks contain about thirty times as much oil as their associated reservoirs.

It is interesting to speculate as to the total quantity of oil in the sedimentary basins of the world, although admittedly such calculations will be somewhat in

error due to the limited amount of data available for such a computation. Weeks (1958) estimates that there are 30 million miles^3 of sedimentary rocks in basins of the continents and continental shelves. These are believed to be composed of approximately 50 per cent shale, 16 per cent carbonate, and 34 per cent sandstone. The total oil in the non-reservoir rock, that is, the shales and carbonates (the latter is considered all non-reservoir for this estimate since the volume of reservoir would be small), can be estimated as follows:

(1) Hydrocarbons in shales

$$\frac{(300)}{(1 \times 10^6)} \frac{(2{\cdot}3)}{(0{\cdot}87)} (30 \times 10^6)(0{\cdot}50) = 11{,}900 \text{ miles}^3$$

The first figure is the average hydrocarbon content in parts per million of the 791 shales from about sixty sedimentary basins in the world (see Table 5). Average densities of 2·3 for shale and 0·87 for oil were used to convert from a weight to volume basis. The volume of shale is shown as one-half 30×10^6 miles^3.

(2) Hydrocarbons in carbonates

$$\frac{(340)}{(1 \times 10^6)} \frac{(2{\cdot}3)}{(0{\cdot}87)} (30 \times 10^6)(0{\cdot}16) = 4320 \text{ miles}^3$$

Total hydrocarbons in non-reservoir rock = 16,220 miles^3.

Weeks has also estimated that the ultimate primary petroleum reserves of the world will be $1{\cdot}5 \times 10^{12}$ barrels. Consequently, total oil in place is probably $3 \times 1{\cdot}5 \times 10^{12}$ barrels. Since there are 26×10^9 barrels per cubic mile, the reservoir oil totals about $4{\cdot}5 \times 10^{12}/26 \times 10^9$ or 173 miles^3.

From these calculations the ratio of the volume of non-reservoir oil to reservoir oil in the sedimentary basins of the world is estimated to be 16,220/173 or 94 to 1.

There is at least one assumption in making this calculation that suggests this ratio is high. The samples analysed could be richer in hydrocarbons than the world's total sedimentary rock because petroleum geologists generally work in the more petroliferous sections of basins and tend to pick the darker sediments when sending in samples for an analysis. There is no way of accurately estimating this error, but in areas that have been sampled objectively such as the Powder River Basin of Wyoming (Table 6) the hydrocarbon content of the shales averages 200 p.p.m., or about one-third less than the values used in the above calculation. If this 200 p.p.m. value were used, the ratio of non-reservoir oil to reservoir oil would be about 60 to 1.

This figure is still broadly qualitative and should not be interpreted as being quantitatively accurate. However, it does show very clearly that the non-reservoir oil still exceeds the reservoir oil in the sedimentary basins of the world by a considerable amount. This means that Nature's method for removing oil does not result in the complete drainage of hydrocarbons from non-reservoir rocks. Instead, an oil pool is the result of a fortunate set of circumstances in which the requisite conditions of reservoir porosity and trap were effective in picking up part of the hydrocarbons that migrated during the period of compaction and lithification. Most of the oil still remains in the non-reservoir beds.

Conclusions

The conclusions of this study are:

(1) Hydrocarbons are found in varying quantities in practically all sedimentary rocks. Associated with the hydrocarbons in rocks are soluble non-hydrocarbons, which are similar to the asphaltic constituents of oil, and an insoluble organic residue (kerogen).

(2) Non-reservoir shales and carbonates contain a wide boiling range of hydrocarbons, comparable to those found in crude oil. However, detailed comparisons of hydrocarbons accumulated in a reservoir with hydrocarbons extracted from the associated source shale indicate that the migrated oil is higher in paraffin and naphthene hydrocarbons and the residual oil higher in aromatic hydrocarbons.

(3) In six recent-sediment areas sampled, no sediment contained as much hydrocarbon as the average ancient sediment.

(4) The greatest variations in the hydrocarbon contents of rocks correlate with lithology and may be due to differences in the environment of deposition.

(5) The per cent hydrocarbon in the total organic matter of rocks appears to increase with increasing rock density. However, metamorphism definitely decreases the hydrocarbon content of a rock.

(6) In a typical sedimentary basin, the Powder River Basin in Wyoming, it was found that there is thirty times as much oil in the non-reservoir rocks as in the reservoir rocks. Estimates for the sedimentary rocks of the entire world also indicate that there is far more non-reservoir oil than reservoir oil in sedimentary basins.

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Étude de la matiere organique dans les roches sedimentaires

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La recherche du caractère de roche-mère de pétrole peut être abordée de différentes manières dont les principales concernent la pétrographie de la partie minérale, l'analyse de la fraction soluble et l'étude de la partie organique insoluble. C'est sur ce troisième point que nous avons entrepris notre travail. Le but à atteindre est de mettre en évidence ce qui caractérise la matière insoluble d'une formation qui a donné du pétrole de celle qui n'en a pas donné.

Nous écartons la possibilité de former des gisements aux quelques p.p.m. d'hydrocarbures rencontrés dans les sédiments actuels. Cette quantité est inférieure à ce que l'on trouve dans les formations anciennes argiloschisteuses ou calcaires.

Parmi les raisons pour lesquelles du pétrole a été produit ou n'a pas été formé, on peut penser que les substances organiques n'étaient initialement pas les mêmes dans les deux cas. On peut aussi supposer qu'une substance initiale convenable n'a pas donné de pétrole parce que les conditions de dépôt n'étaient pas favorables.

On conçoit l'influence du milieu favorable comme une "réduction" des substances oxygénées. Certaines (telles que cires et corps gras) auraient subi la réduction jusqu'aux hydrocarbures, et les autres (amino acides, par exemple) auraient été "réduites" a un degré moindre. Si dans la formation du pétrole on admet une action catalytique des argiles, il se produit des transformations plus ou moins profondes des divers composants de la substance organique.

De toute façon, quelque soit le processus de formation du pétrole, nous admettons que le reste des substances de la formation productrice, n'a pas la même composition que la matière de la formation qui n'a pas donné de pétrole.

Théoriquement, on pourrait mettre en évidence ces diverses compositions chimiques s'il était possible d'analyser la matière organique pure. Mais il est difficile de la séparer de son support minéral par une opération mécanique. On est obligé généralement d'opérer la destruction des minéraux au moyen d'acide chlorhydrique et fluorhydrique. Cette action énergique ne se fait pas sans altérer fortement la partie organique. On s'en rend compte en particulier d'après la forte diminution de la teneur en azote. La matière organique séparée, à notre avis, ne représente pas la substance contenue dans le sédiment.

Force reste donc de trouver une méthode qui s'applique à la roche elle-même. On peut déterminer d'une façon assez exacte le carbone organique et l'azote. Mais ces deux valeurs sont insuffisantes pour différencier la nature de la substance organique.

Parmi les travaux antérieurement exécutés sur la caractérisation de la nature organique des sédiments, nous avons retenu ceux de Himus et de ses collaborateurs. Ils ont étudié les produits de l'oxydation en milieu aqueux par le permanganate

de potassium. Les acides oxalique et des polyacides benzène carboniques ont été trouvés en différentes proportions. Ce procédé paraissait intéressant, mais trop long pour être appliqué sur un grand nombre d'échantillons comme cela est nécessaire dans une campagne de prospection. Après plusieurs essais, nous avons alors adopté une méthode basée sur un critère de caractérisation de la substance organique restant dans la roche au cours d'oxydations successives et progressives.

Ce critère utilisé est le rapport PR/C. Le pouvoir réducteur, PR, théoriquement, devrait représenter la quantité d'oxygène qui est nécessaire pour oxyder complètement la matière organique, c'est à dire pour faire passer le C en CO_2, H en H_2O et N en NO_2. Théoriquement, il donnerait une image indirecte de l'état de réduction de la substance puisque à carbone égal, le PR serait d'autant plus élevé que la teneur en hydrogène serait plus grande. C'est pourquoi le rapport PR/C serait un critère.

La méthode de détermination de PR d'après Trask, si elle oxyde toute la matière organique, en réalité ne transforme pas la substance intégralement en CO_2 et H_2O mais donne des composés acides tels que les acides benzène carboniques.

Cet inconvénient, quand à la valeur absolue de PR, n'est qu'apparent. Il est en effet possible que la formation d'acides benzène carboniques soit due à des molécules complexes cycliques existant dans la substance initiale et par ce fait, le PR reflète en partie la complexité de la substance, cela se traduit surtout au cours de l'oxydation sélective pendant laquelle les molécules cycliques sont évidemment attaquées en dernier lieu avec une baisse relative correspondante du PR. La courbe de PR/C au cours de l'oxydation traduira donc l'aspect moléculaire de la substance. Des études sont en cours pour élucider ces phénomènes d'oxydation.

La sélectivité de l'oxydation a déjà été abordée en se basant sur le rapport C/N. Sur le graphique no. 1 nous avons porté l'oxydation sélective d'après PR/C et en parallèle le rapport C/N.

En général, ce rapport augmente au cours de l'oxydation ce que l'on doit attribuer à une résistance plus grande de certaines molécules azotées et ce qui démontre que l'oxydation est sélective, au moins en ce qui concerne ce genre de molécules.

Cette augmentation du rapport C/N ne se fait d'ailleurs pas dans les mêmes proportions avec tous les échantillons.

Mode Operatoire

Les roches préalablement réduites en morceaux de 2 à 4 mm, sont traitées au chloroforme pour extraire la partie soluble et ne laisser que la matière organique insoluble. Après séchage, l'échantillon est broyé de façon à passer à travers le tamis 180.

Les roches sont ensuite soumises à une attaque chlorhydrique avec une solution d'acide à 10% puis lavées abondamment pour enlever toutes traces d'acide et de chlorures.

Pour que les conditions d'oxydation soient aussi semblables que possible d'un échantillon à l'autre, il importe que la quantité de matière organique par rapport à la quantité d'oxydant soit à peu près constante. De plus, à chaque étape de

l'oxydation, il faut pouvoir déterminer avec assez d'exactitude le carbone organique et le pouvoir réducteur, ce qui ne peut être fait sur des quantités infimes de substance organique. Ceci implique que l'échantillon initial contienne une quantité de matière organique appréciable. Une teneur d'environ 3% en carbone organique dans l'échantillon initial est très convenable; au-dessous de 1% la courbe d'oxydation devient plus difficile à établir.

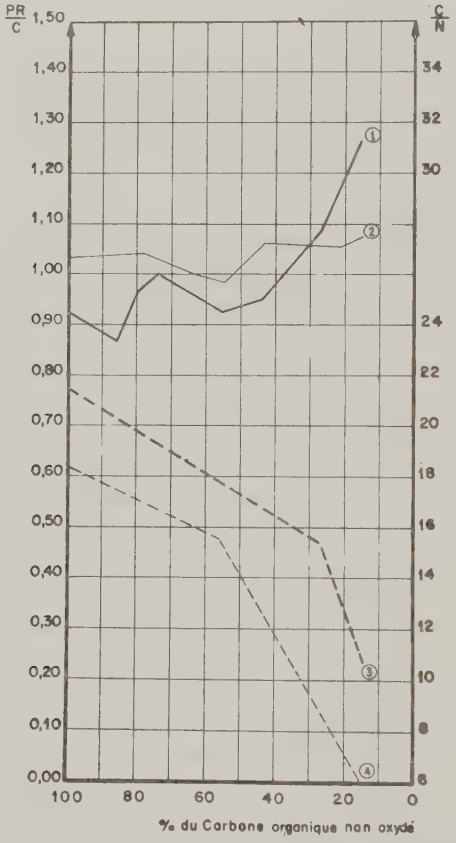

Fig. 1

Si l'échantillon contient plus de 3% de carbone organique on le dilue avec du kaolin en ayant soin d'homogénéiser le mélange.

Le carbone organique est déterminé par combustion dans un four électrique dans un courant d'oxygène. Le volume de CO_2 formé est mesuré.

Dans une dizaine d'erlenmeyers de 250 cm³ avec bouchon émeri, on introduit 1,5 g d'échantillon puis 2 à 3 cm³ d'acide sulfurique 0,15 N. Quand la roche est entièrement mouillée, on ajoute 3 à 4 cm³ de solution de permanganate à 3%.

Les erlenmeyers sont placés dans une étuve à 60°C; on les laisse jusqu'à ce que le permanganate soit réduit. Le premier échantillon est alors enlevé pour analyse; dans les autres on ajoute une nouvelle quantité de permanganate.

L'opération est poursuivie jusqu'à ce que 80 à 90%, de la matière organique soient oxydés.

Le contenu des erlenmeyers est récupéré dans de l'eau distillée et traité par un courant de SO_2 pour enlever l'oxyde de manganèse formé. On filtre sur creuset en verre fritté taré, on lave à l'eau chaude. Après séchage et pesée, la roche est broyée dans un petit mortier et soigneusement homogénéisée. On procède alors à la détermination du carbone organique par voie sèche et du pouvoir réducteur (méthode de Trask).

Resultats

Les essais ont porté sur des échantillons de caractères lithologiques différents tels que roches siliceuses, schisteuses, calcaires et d'âges géologiques divers. Pour

Tableau 1. Propriétés des échantillons après extraction au chloroforme (avant le traitement à l'acide chlorhydrique)

No.	Nature	Extrait chlorof.	C Minéral	C Organique	N Total	*PR* Corrigé	C/N	*PR/C*
	Roches siliceuses							
1375	Diatomite de S.—Brahim	0,29	2,94	2,25	0,22	2,16	10,1	0,94
1771	Diatomite de la Veyssière	1,61		9,71	0,43	8,74	22	0,90
2942	Diatomite de Breloh	1,47		9,01	0,25	7,38	36	0,82
	Roches schisteuses							
1227	Toarcien de Suderbruch	1,44	3,27	6,46	0,23	6,08	28,8	0,94
1584	Toarcien de Courgivaux	1,66	2,90	5,19	0,28	4,91	22	0,94
3085	Gothlandien Sylvain Shale	0,15	4,99	4,15	0,47	4,32	8,8	1,04
2613	Gothlandien Sahara	0,16	5,50	7,06	0,54	6,29	13	0,89
1848	Dévonien Sahara	0,06		2,28	0,28	1,14	8,1	0,51
322	Permien Saint Hilaire	1,74		20,06	0,64	20,08	31	1,00
3577	Duvernay (Canada)	1,38	5,28	8,09	0,45	7,79	17,9	0,96
3767	Woodford (U.S.A.)	0,36		4,01	0,20	3,06	20	0,76
3175	Rifle-Ridge Green River	2,05		10,3	0,39	11,15	26,4	1,08
3174	Chattanooga (U.S.A.)	0,19		4,31	0,26	2,59	16,5	0,60
	Roches calcaires							
3644	La Luna	0,35	7,57	5,26	0,28	5,48	19	1,04
1373	Saint-Champ	4,29	10,2	6,29	0,22	6,86	27,4	1,09
3646	Seefeld (Autriche)	3,12	5,02	21,57	0,24	22,53	89,8	1,04
	Sédiments actuels							
3549	Vase de la Baltique		0,45	5,47		4,92		0,90
1478	Acides humiques			49,14	3,30	40,3	14,8	0,82

tester la méthode, nous avons cherché à nous procurer des échantillons de formations que les géologues ont tout lieu de penser être roche-mère. C'est ainsi que nous avons étudié la diatomite de Sidi-Brahim, le toarcien de Suderbruch, le gothlandien de Sylvan Shale, les schistes de Woodford et de Duvernay, le calcaire de La Luna.

Par ailleurs, nous avons analysé un certain nombre d'échantillons provenant de France et d'autres pays. Parmi ceux-ci, nous citerons ici ceux qui par leur caractère spécial de sédimentation ou milieu, nous paraissent présenter un intérêt. L'analyse globale est indiquée dans le Tableau 1.

Pour plus de commodité, la présentation des résultats est faite d'après la nature lithologique de la roche.

Roches siliceuses (*Fig.* 2)

(a) Diatomite marine de Sidi Brahim (Algérie). Elle semble être la roche-mère du petit gisement de Ain Zeft (1). On voit sur la courbe 1 qu'elle donne une courbe d'oxydation ascendante.

(b) Diatomite continentale de La Veyssière (France) (courbe 2). Elle provient d'un ancien lac dans la région volcanique du Massif Central et par conséquent n'a jamais été roche-mère. Elle contient une forte proportion de matière organique.

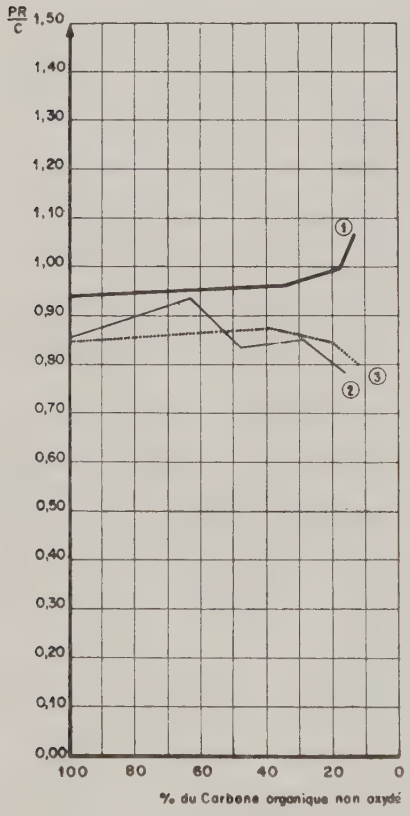

Fig. 2

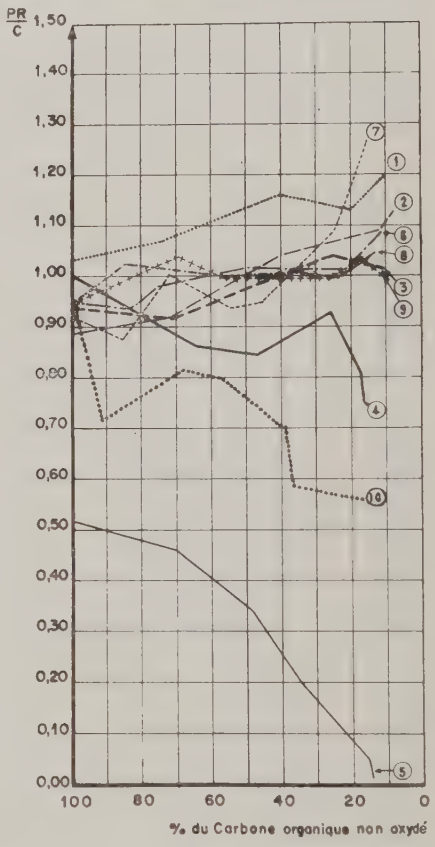

Fig. 3

Sa courbe d'oxydation est descendante. Il y a ici une différence d'allure très nette avec la courbe précédente.

(c) Diatomite de Breloh (en Allemagne) (courbe 3). Elle provient d'un ancien lac glaciaire; elle n'est donc pas roche-mère. Sa courbe d'oxydation est descendante comme la précédente et son allure s'écarte nettement de celle de la roche-mère de Sidi-Brahim (courbe 1).

Roches shisteuses (*Fig.* 3)

(a) Sylvan Shale. Cette formation du Gothlandien est généralement considérée comme une bonne roche-mère. Sa courbe d'oxydation est nettement ascendante (courbe 1).

(b) Un schiste du Gothlandien du Sahara (courbe 2) donne aussi une courbe semblable. Le Gothlandien du Sahara est considéré comme une roche-mère possible, sans que cela ait été démontré jusqu'à présent.

(c) Schistes à posidonomies du toarcien de Suderbruch (Allemagne). Cette formation est considérée comme une roche-mère, d'autant plus qu'elle est même productive. Elle a l'aspect d'un schiste riche en matière organique. Sa courbe d'oxydation est ascendante (courbe no. 3).

(d) Pour comparer nous avons étudié un échantillon de toarcien du Bassin de Paris, du sondage de Courgivaux. La courbe d'oxydation (no. 6) est aussi donnée ascendante. Etant donné la présence du pétrole dans plusieurs niveaux du Jurassique, il n'est pas exclu que le toarcien a joué un rôle.

(e) Le schiste du permien de St. Hilaire (France) donne une courbe descendante (no. 4). C'est une formation continentale qui pour le moment ne semble pas en relation avec un gisement de pétrole. Ce schiste donne cependant au chloroforme, jusqu'à 1,74% d'extrait qui contient lui même 75% environ d'hydrocarbures.

(f) Un échantillon de schiste du dévonien du Sahara ayant au départ un rapport PR/C nettement inférieur à 0,80 donne une courbe d'oxydation (no. 5) très fortement descendante.

Cette indication, défavorable au point de vue roche-mère, n'est évidemment valable que pour l'échantillon étudié. Le dévonien a une épaisseur de plusieurs centaines de mètres, et dans cet ensemble il peut présenter un caractère différent.

(g) Le schiste de Duvernay (Canada) qui est considéré par plusieurs géologues comme une roche-mère possible, donne une courbe (no. 7) fortement ascendante.

(h) L'échantillon de schiste de Woodford (U.S.A.) donne également une courbe ascendante (no. 8). Il peut être considéré comme une roche-mère possible.

(i) Le schiste de Rifle-Ridge (Green River) d'origine continentale considéré comme roche-mère. La courbe d'oxydation no. 9, bien que n'étant pas très ascendante, permet cependant de conclure que cette formation a pû donner du pétrole.

(k) Un échantillon de schiste de Chattanooga (U.S.A.) donne une courbe descendante (no. 10) qui n'a pas l'allure de celle d'une roche-mère.

Roches calcaires (*Fig.* 4)

(a) La Luna (Vénézuéla). Cette formation est supposée par de nombreux géologues être à l'origine de plusieurs gisements de pétrole. Elle constitue donc pour nous un repère important dans notre étude. Elle donne une courbe d'oxydation très fortement ascendante (courbe no. 1).

(b) Calcaire du Kimeridgien de St Champ (France). Il s'agit d'une formation marine déposée dans une sorte d'atoll (2). Elle se présente sous forme d'un sédiment fin en lits foncés riches en matière organique et en lits clairs plus pauvres. On peut en extraire une substance visqueuse très riche en soufre et ayant un caractère fortement acide, n'ayant probablement jamais passé par le stade pétrole; les conditions de dépôt n'ont sans doute pas été assez réductrices. La courbe d'oxydation (no. 2) a aussi une allure particulière. Le rapport PR/C très élevé au départ diminue rapidement puis demeure ensuite sensiblement constant mais toujours supérieur à 0,80.

(c) Seefeld (Tyrol Autriche). Il s'agit d'une formation lagunaire dans la dolomie du Trias. L'extrait, comme le précédent, a un caractère fortement acide et il est très sulfuré. On peut voir sur la Fig. 3 que la courbe d'oxydation est analogue à celle de St Champ.

Sédiments actuels (*Fig.* 5)

(a) Il était intéressant de voir le comportement des sédiments marins actuels vis à vis de la méthode. Nous avons utilisé des vases provenant de la mer Baltique, qui est un milieu peu salé.

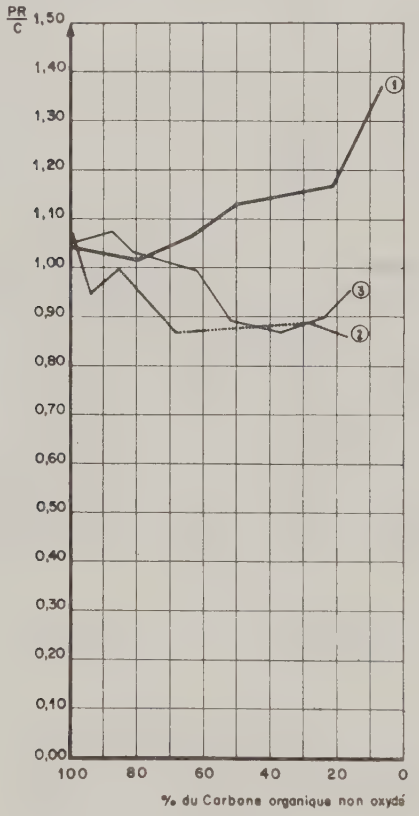

Fig. 4

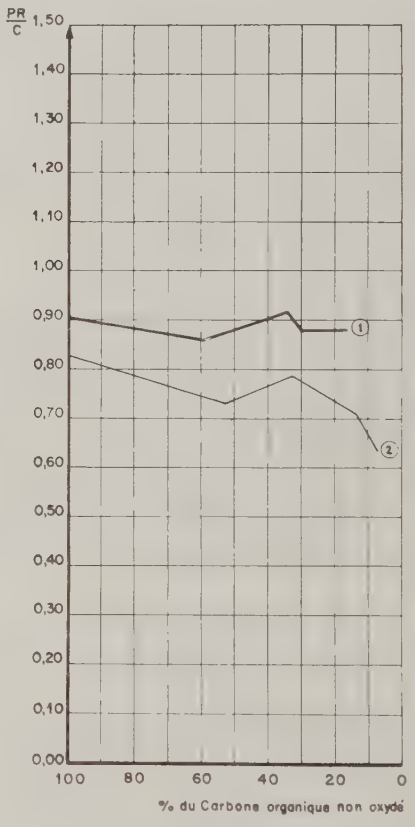

Fig. 5

La courbe d'oxydation a une allure assez proche d'une droite, c'est à dire que la matière organique ne se différencie pas, l'ensemble de ses composants s'oxyde d'une façon continue. On peut interpréter ceci comme le fait que la substance initiale n'est pas encore transformée, c'est à dire n'a pas subi de réduction ou de diagénèse.

(b) Les acides humiques étant un autre constituant des sédiments, nous les avons aussi "essayés". Ils donnent une courbe descendante avec des valeurs inférieures à 0,80.

Conclusions

Si le mécanisme de l'oxydation sélective des matières organiques des sédiments n'est pas encore connu, nous pouvons cependant, par cette méthode, établir des différences très nettes suivant l'origine du matériel organique et de ses conditions de dépôt.

Les courbes d'oxydation ne différencient pas les dépôts marins des dépôts continentaux. On voit par exemple, une différence de comportement des dépôts marins en milieu réducteur (roches mères) et en milieu lagunaire (St Champ et Seefeld). Les vases actuelles présentent une autre allure de courbe.

D'autre part, le schiste continental de Rifle-Ridge peut être considéré comme roche-mère.

En résumé, nous obtenons trois types de courbes d'oxydation: (i) courbe ascendante = caractéristique des roche-mères; (ii) courbe descendante = caractéristique des formations qui n'ont pas donné de pétrole; (iii) courbe sensiblement horizontale = caractéristique des vases marines actuelles.

Il existe encore une variante pour les formations lagunaires.

Si la méthode proposée n'apporte pas une preuve absolue qu'un sédiment a fonctionné comme roche-mère, elle permet d'écarter ceux qui n'ont pas été générateurs de pétrole, et parmi les autres, elle indique des probabilités supplémentaires pour qu'on leur accorde de l'intérêt.

On peut ainsi dans un bassin déterminé, sélectionner certaines formations à partir desquelles, on calcule l'apport organique. On peut alors se faire une idée de la quantité de pétrole qu'elles ont pu fournir. De telles indications expliqueraient sans doute, pourquoi une formation connue ne renferme que des traces de pétrole. Elles peuvent aussi expliquer la concentration de l'huile dans une certaine partie d'un bassin.

Remerciements—Il nous est agréable de remercier les personnes et les sociétés qui ont bien voulu nous fournir des échantillons pour cette étude: MM. Debyser (I.F.P.), Hanson (Mellon Institute), Ortynski (S.N. Repal), H. Smith (Bureau of Mines), les Sociétés Brigitta (Allemagne), Magnolia Petroléum Co. (U.S.A.), R.A.P. et S.N.P.A. (France).

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Geochimica et Cosmochimica Acta, 1961, Vol. 22, pp. 58 to 64. Pergamon Press Ltd. Printed in Northern Ireland

Significance of hydrocarbons in sediments and petroleum

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Abstract—Sediments and crude oils contain the same types of hydrocarbons. This analogy indicates that petroleum is derived from sedimentary organic matter. The close resemblance of hydrocarbons in sediments and crude oils to the products of living organisms indicate that compounds pass from living things into petroleum deposits without appreciable chemical change. Major transformations of organic matter into petroleum-like compounds do not appear to be an essential function of source beds. Neglecting bacterial modifications and rearrangement of unsaturated products that apparently occur shortly after deposition of plant and animal remains in sediments, the important processes in forming petroleum deposits are probably physical in nature. Sediments in general rather than unusual sediments are seemingly the true "source rocks" of petroleum.

Introduction

Cox (1946) and Stevens (1956) have expressed the generally accepted view that crude oils are accumulations of naturally produced hydrocarbons. For accumulations or concentrations to occur, there must be a source of the material that is concentrated. In the case of petroleum, these sources have been arbitrarily called source beds or source rocks.

Before the recent development and improvement of mass, infra-red, and ultra-violet spectrometers and chromatographic procedures, the techniques employed in sediment studies did not permit the detection of hydrocarbons in most sediments (Trask, 1932). Although, as noted by Whitmore (1946), hydrocarbons were known products of plants and animals and thus should be in sediments, the failure to recognize sediment hydrocarbons led to a mistaken belief that they were destroyed completely by bacterial action in near surface sediments (Cox, 1946). This misconception, based on the best experimental data then available, removed any direct relationship between hydrocarbons in plants or animals and in petroleum, making it necessary to assume that crude oil hydrocarbons were produced only in a very restricted group of sediments called source rocks.

Recent investigations by Smith (1952, 1954), Stevens *et al.* (1956) and Meinschein (1957), show that hydrocarbons are present in nearly all sediments. Although the concentrations of hydrocarbons in recent sediments vary, the concentrations are in all cases quite low. Despite the low concentration of hydrocarbons inherited or obtained in the early depositional history, there are apparently sufficient hydrocarbons in sediments to supply several times over all the crude oil believed to exist in Nature. These findings suggest that sediments in general are source beds.

Methods

Samples

Recent marine sediments were collected by rotary rigs off Jefferson Parish, Louisiana, in the Gulf of Mexico at Grand Isle Block 18 Dome. The Oklahoma crude oil was obtained from the Walker Heirs Well no. 4 in Seminole County, and

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the oil was Pennsylvanian in age. The Texas crude oil was from the F. M. Hearn Estate no. 1 Well in Harrison County. The latter oil was Cretaceous in age. Data on the samples described in a previous paper (MEINSCHEIN, 1959) were considered in the preparation of this article.

Extraction

The Grand Isle sediments were extracted by stirring them with two different portions of a boiling solvent consisting of seventy parts benzene, fifteen parts acetone, and fifteen parts methanol by volume. Each extraction lasted 16 hr, and 2 ml of solvent per g of sediment was used per extraction. Other extractions were performed as described by MEINSCHEIN (1959).

Chromatography, spectroscopy and interpretation of data

The procedures and methods used in this investigation were described by MEINSCHEIN (1959) and MEINSCHEIN and KENNY (1957).

DISCUSSION

Before the origin or source of a natural product or a substance can be determined, the product or substance must be identified. Petroleum is a complex mixture of chemical compounds derived from organic matter. The absolute identification of a crude oil would require the quantitative and qualitative analyses of its chemical constituents. Even with modern instruments and techniques a complete analysis of a crude oil is either impossible or economically infeasible, but the identities of a number of the major hydrocarbon components of crude oils and sediments have been obtained (MEINSCHEIN, 1959). The identities of these components have made it possible to establish relationships between naturally occurring hydrocarbons and the products of living organisms. These relationships provide an indication as to the origin of petroleum and the nature of source rocks.

Sediment and petroleum hydrocarbons

All the hydrocarbons or types of hydrocarbons that have been identified in sediments have been shown or strongly indicated to be the same compounds that are found in crude oils (MEINSCHEIN, 1957, 1959). The principal differences observed between hydrocarbons from these sources are distributional differences. The structural similarities and a distributional difference between different types of saturated hydrocarbons from a recent marine sediment and two unrelated crude oils are indicated clearly by the plots of mass spectra as shown in Figs. 1–7.

These figures show the plots of the even mass number C_{18} through C_{32} ion peak heights for the saturated hydrocarbon fractions of a Recent marine sediment extract, a crude oil from Oklahoma, and the alumina chromatographic fractions of a Texas crude oil. These mass spectral plots indicate the amounts and molecular weight distributions of the various types of hydrocarbons in these fractions. The x groups plotted in the different figures correspond to the values of x in the general hydrocarbon formula C_nH_{2n+x} for the seven types of saturated hydrocarbons starting with paraffins ($x = 2$) and ending with hexacyclics ($x = -10$). The dominant hydrocarbon type plotted in each figure is noted.

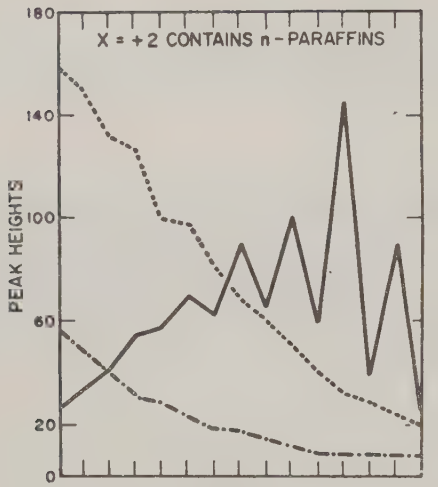
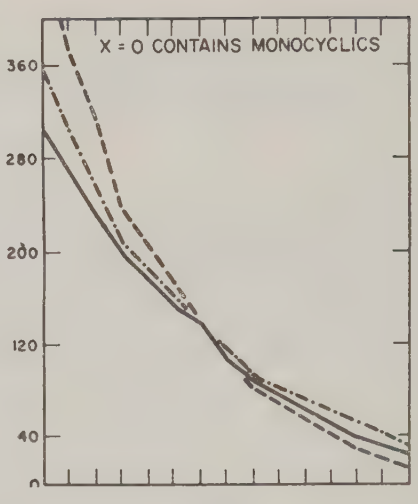


Fig. 1



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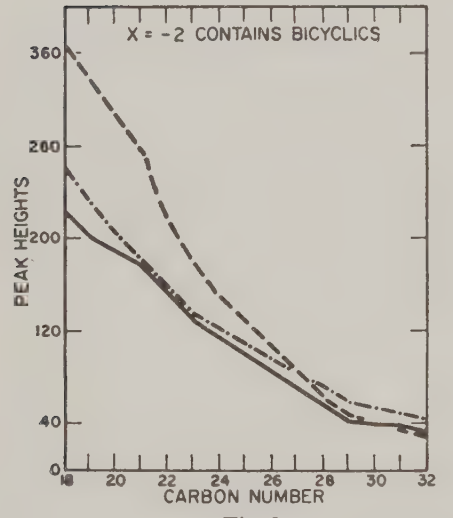

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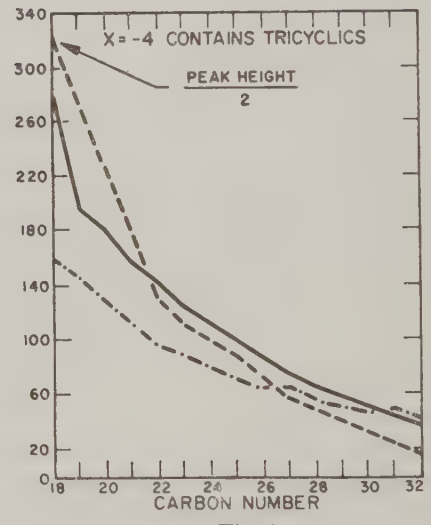


Fig. 4

Saturated hydrocarbons plot of parent peaks in mass spectra

With exception of the *n*-paraffins that obviously have a distribution in sediments that is different than in crude oils, as noted in previous publication (Stevens *et al.*, 1956; Evans *et al.*, 1957; Meinschein, 1957, 1959), the plots of the other saturated hydrocarbons in the sediment and crude oils are remarkably similar. The sediment and crude oil plots resemble each other as closely in types and molecular weight distribution as do the plots of the two crude oils.

The structural similarities and the distributional differences between the aromatic hydrocarbons in sediments and those in crude oils can be determined from their ultra-violet and mass spectra (Meinschein, 1959). The ultra-violet

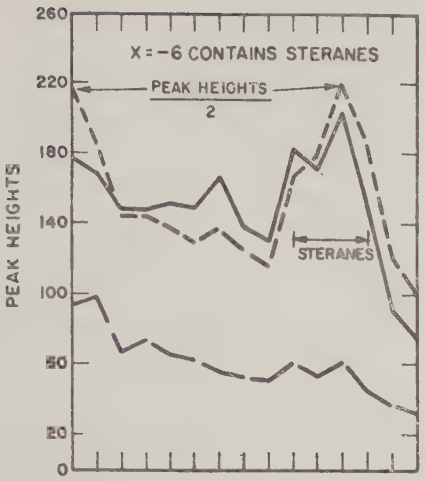
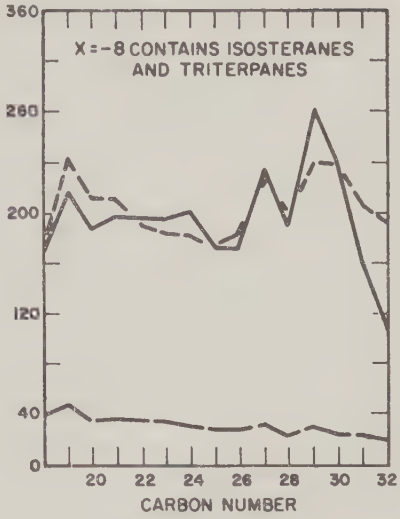


Fig. 5



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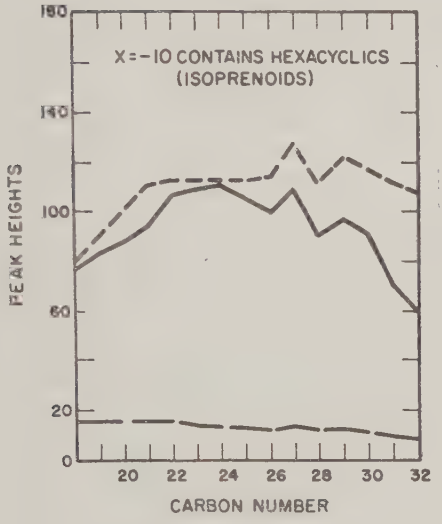
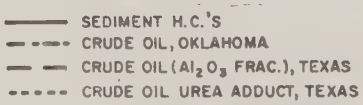


Fig. 7



Saturated hydrocarbons plot of parent peaks in mass spectra

spectra of chromatographic fractions of aromatic hydrocarbons from a recent marine sediment extract and a crude oil are shown in Figs. 8–11.

Figs. 8 and 9 show that alkyl- and *cyclo*alkyl-benzenes and -naphthalenes from sediments and a crude oil are very similar. The mass spectra of these compounds show further that the molecular weight distributions of these benzenes and naphthalenes from sediments and crude oils are equally as similar.

Figs. 10 and 11 show that the distributions of polycyclic aromatics containing three or more condensed benzenoid rings in sediments differ from those in crude

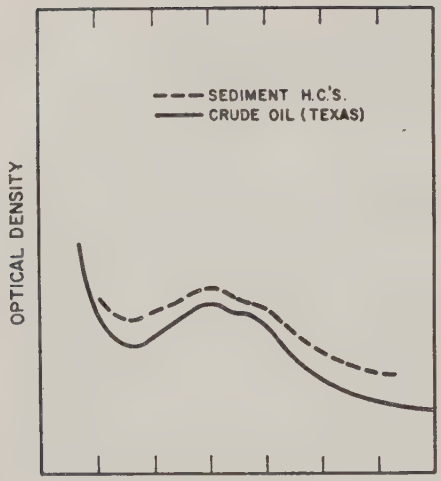


Fig. 8

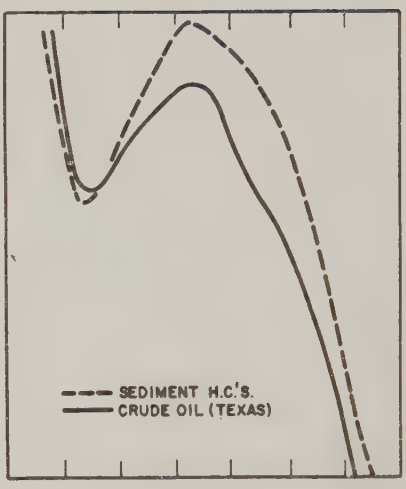


Fig. 9

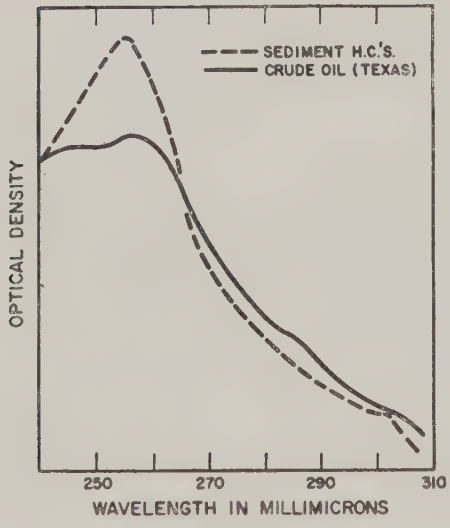


Fig. 10

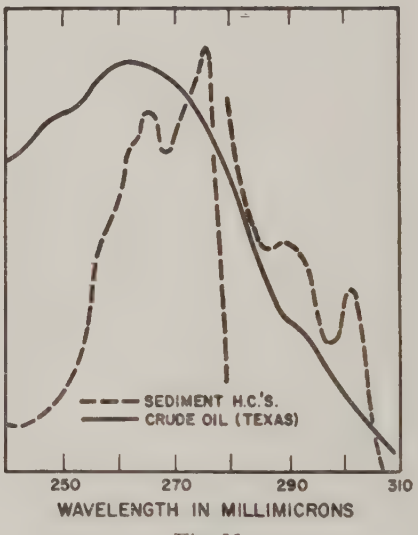


Fig. 11

Ultraviolet spectra of aromatic fractions

oils. A detailed comparison of these distributions has been made previously (Meinschein, 1957, 1959). Summarizing briefly, polycyclic aromatics in crude oils differ in the *relative abundances* of compounds and in *complexity* from those in recent sediments. Alkyl-substituted polycyclic aromatics are more abundant in crude oils; whereas the unsubstituted compounds are more abundant in the sediments. Crude oil polycyclic aromatic fractions are more complex than these fractions from a particular recent marine sediment because crude oils are accumulations of hydrocarbons from many sediments and the complement of specific hydrocarbons vary from sediment to sediment.

The relationship between the hydrocarbons in sediments and in petroleum

Organic extracts of sediments and crude oils resemble one another in many respects, but crude oils differ in certain respects from all other types of deposited organic substance. The liquid nature of petroleum and its great solubility in organic solvents leave no doubt that crude oils are composed of a far greater proportion of low molecular weight compounds than all other composite naturally produced liquid or solid organic matter living or dead. Elemental analyses show that sediment extracts other than those from petroleum reservoirs contain several times the amount of organic non-hydrocarbons per unit weight as does the average crude oil. The significant differences that exist between petroleum on the one hand and other deposits or matter on the other hand show that crude oils are selective accumulations.

An understanding of the manner in which the petroleum accumulation process is selective is necessary to the chemical identification of source rocks. This necessity presents a problem because the composition of the source matter is needed so that the selective nature of the accumulation process can be determined. Fortunately, a logical solution to this problem is provided by present knowledge.

Living organisms are the primary source of all organic matter. The structures of many hydrocarbons from sediments and from crude oils show that these compounds are obtained from plant and animal products (MEINSCHEIN, 1959). The fact that the structures and molecular weights of the hydrocarbons in crude oils that are millions of years old are the same as those in recent sediment hydrocarbons attests to their great stability in sedimental environments.

Present data do not show whether petroleum constituents are produced primarily in living things or in young sediments. It is known that organisms do contain petroleum-type hydrocarbons and that the hydrocarbons in recent sediments do reflect the distributions of either the hydrocarbons or of their obvious source compounds in living things (MEINSCHEIN, 1959). The distribution of the hydrocarbons in recent sediments indicate that they were formed by minor modification of a select group of compounds produced by plants and animals. These modifications may or may not have taken place in the source organisms, but the hydrocarbons in sediments are most certainly not primarily the products of random and extensive chemical conversions of organic matter. The structures of the hydrocarbons in sediments and in petroleum and the distributions of hydrocarbons in sediments would thus indicate that these compounds were produced principally by selective processes involving living organisms.

The differences between sediment extracts and crude oils and the differences in distributions between the hydrocarbons in recent sediments and those in petroleum are differences in the relative amounts of compounds in the extracts and in the crude oils. These are physical differences. Neither is it essential to petroleum formation nor do existing data show that chemical transitions other than those carried out by or in living organisms play an important role in the origin of petroleum. The differences in distribution that are known to exist between the hydrocarbons in sediments and those in crude oils can be explained by the accumulation process proposed by BAKER (1959).

BAKER'S investigations indicate that crude oils are accumulated by a ground

water solution and release process. Water and minerals represent the common continuous phases in most sediments. Dispersed hydrocarbons must move through one or both of these phases to reach reservoir rocks. Water, being liquid, can provide greater mobility than can solid minerals to hydrocarbons, and water should have transported a major portion of source materials to petroleum deposits. Solution in and release from water explains in a general way how crude oils can be formed from hydrocarbons derived from living products. Recent data clearly support the thesis that crude oils are concentrates of sedimental organic matter that was selectively accumulated by subterranean waters.

Although water was apparently the most efficient agent available and served to accumulate most petroleum, water is a poor solvent for the substances in crude oil. Sediments containing only a few parts per million of petroleum source materials may have saturated all ground waters associated with these sediments and have participated fully in the petroleum forming processes.

Since nearly all sediments contain hydrocarbons, most sediments did contain hydrocarbons in excess of the amounts that subterranean waters could dissolve and carry to reservoirs. Thus, most sediments are apparently capable of supplying all the hydrocarbons that can be handled by the medium that concentrates hydrocarbons in petroleum deposits, and sediments in general rather than particular or unusual sediments are probably the true source of petroleum.

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